Analytical Methods for Drinking Water

Advances in Sampling and Analysis

PHILIPPE QUEVAUVILLER
European Commission, Brussels, Belgium

K. CLIVE THOMPSON
ALcontrol Laboratories
South Yorkshire, UK

John Wiley & Sons, Ltd

 John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester,
West Sussex PO19 8SQ, England

Telephone (+44) 1243 779777

Email (for orders and customer service enquiries): cs-books@wiley.co.uk
Visit our Home Page on www.wileyeurope.com or www.wiley.com

Other Wiley Editorial Offices

John Wiley & Sons Inc., 111 River Street, Hoboken, NJ 07030, USA

Jossey-Bass, 989 Market Street, San Francisco, CA 94103-1741, USA

Wiley-VCH Verlag GmbH, Boschstr. 12, D-69469 Weinheim, Germany

John Wiley & Sons Australia Ltd, 42 McDougall Street, Milton, Queensland 4064, Australia

John Wiley & Sons (Asia) Pte Ltd, 2 Clementi Loop #02-01, Jin Xing Distripark, Singapore 129809

John Wiley & Sons Canada Ltd, 22 Worcester Road, Etobicoke, Ontario, Canada M9W 1L1

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Library of Congress Cataloging-in-Publication Data

Quevauviller, Ph.
Analytical methods for drinking water : advances in sampling and analysis / Philippe Quevauviller, K. Clive Thompson.
p. cm.
Includes bibliographical references and index.
ISBN-13: 978-0-470-09491-4 (cloth : alk. paper)
ISBN-10: 0-470-09491-5 (cloth : alk. paper)
1. Water – Analysis. 2. Drinking water – Analysis. 3. Drinking water – Government policy – Europe. 4. Drinking water – Government policy – United States. I. Thompson, K. C. (Kenneth Clive), 1944– II. Title.

TD380 .Q48 2006
363 .6′1—dc22 2005010209

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

ISBN-13: 978-0-470-09491-4 (HB)
ISBN-10: 0-470-094915 (HB)

Typeset in 10.5/12.5pt Times New Roman by TechBooks, New Delhi, India
Printed and bound in Great Britain by TJ International, Padstow, Cornwall
This book is printed on acid-free paper responsibly manufactured from sustainable forestry in which at least two trees are planted for each one used for paper production.

Dedication

This book is dedicated to the memory of A. L. Wilson (1929–1985).

Antony Leslie (Tony) Wilson was born in Brighton in 1929 and educated at Vardean Grammar School and Kings College, London, where he took an honours degree in chemistry. He worked for eighteen years at the Atomic Energy Research Establishment, Salwick and the Central Electricity Research Laboratories, Leatherhead, before joining the Water Research Association at Medmenham—later to become a constituent laboratory of the Water Research Centre—in 1968. He remained with the Centre until his retirement in 1980, when he held the position of Manager of the Analysis and Instrumentation Division.

His considerable reputation as an analytical chemist was the product of a prodigious capacity for work and the painstaking application of his considerable intellect, not only to the development of a wide range of methods, but also to the fundamental principles of analysis quality control. His work on the latter was especially pioneering and its importance has become very widely recognised.

His approach to the specification and assessment of analytical performance and to the control of analytical errors formed the basis of the standard practices of both the electricity generating and water industries in the U.K. Over the years the former Department of the Environment, in its Harmonised Monitoring Scheme, and the World Health Organization, in its Global Environment's Standing Committee of Analysts have incorporated his ideas on performance characterisation in their published methods.

In 1975 he was awarded the Louis Gordon Memorial Prize for the best paper of the year in the journal *Talanta* (one of a series in which he drew together in a coherent manner the important factors to be considered in characterising the performance of analytical methods).

It is considered very fitting that this book dealing with various aspects of water quality should be dedicated to such an illustrious and dedicated individual.

Contents

Series Preface

Water is a fundamental constituent of life and is essential to a wide range of economic activities. It is also a limited resource, as we are frequently reminded by the tragic effects of drought in certain parts of the world. Even in areas with high precipitation, and in major river basins, overuse and mismanagement of water have created severe constraints on availability. Such problems are widespread and will be made more acute by the accelerating demand on freshwater arising from trends in economic development.

Despite of the fact that water-resource management is essentially a local, river-basin based activity, there are a number of areas of action relevant to all or significant parts of the European Union and for which it is advisable to pool efforts for the purpose of understanding relevant phenomena (e.g. pollution, geochemical studies), developing technical solutions and/or defining management procedures. One of the keys for successful cooperation aimed at studying hydrology, water monitoring, biological activities, etc., is to achieve and ensure good water quality measurements.

Quality measurements are essential for demonstrating the comparability of data obtained worldwide and they form the basis for correct decisions related to management of water resources, monitoring issues, biological quality, etc. Besides the necessary quality control tools developed for various types of physical, chemical and biological measurements, there is a strong need for education and training related to water quality measurements. This need has been recognized by the European Commission, which has funded a series of training courses on this topic that cover aspects such as monitoring and measurement of lake recipients, measurement of heavy metals and organic compounds in drinking and surface water, use of biotic indexes, and methods of analysing algae, protozoa and helminths. In addition, a series of research and development projects have been or are being developed.

This book series will ensure a wide coverage of issues related to water quality measurements, including the topics of the above mentioned courses and the outcome of recent scientific advances. In addition, other aspects related to quality control tools (e.g. certified reference materials for the quality control of water analysis) and monitoring of various types of waters (river, wastewater, groundwater) will also be considered.

This book, *Analytical Methods for Drinking Water: Advances in Sampling and Analysis* is the fourth in the series; it has been written by policymakers and scientific experts in drinking water analytical science and offers the reader an overview of drinking water policies and examples of analytical research directly supporting these policies.

The Series Editor – Philippe Quevauviller

Preface

Drinking water policies and research are intimately linked. It is thanks to the scientific progress made over the last 25 years in identifying and controlling toxic products in drinking water that regulations have developed in such a way that the protection of public health from waterborne diseases has drastically improved. The integration of research outputs into the policy-making progress requires close cooperation among the scientific and policy communities, which is not always straightforward. In the US, drinking water research is an integral part of the US Environmental Protection Agency's base research programme, meaning that research is directly feeding the policy process. In Europe, links have also been established among research and policy development, albeit in a less integrated way. Exchanges between scientific and policy-making communities certainly represent key elements of progress for better environmental protection. In this respect, analytical developments linked to drinking water are at the core of the science-policy debate.

This book reflects this awareness by joining recent analytical developments with policy considerations. The first chapter gives an overview of EU and US drinking water policies, as well as on standardization. Analytical developments are described in depth in Chapter 2, focusing on bromate in drinking water. The third chapter deals with the development of a sampling protocol for determining lead in drinking water, thus mixing analytical development with standardization needs. Finally, Chapter 4 focuses on standardization aspects (pre-normative research) related to materials in contact with drinking water.

This book has been written by experts in the field of drinking water policy and analysis. It does not pretend to give an exhaustive view of drinking water analytical developments, but rather illustrates recent scientific advances in this field, which have contributed to policy development. The gathered information will be of direct use to policymakers, water scientists, researchers and analytical laboratories.

Philippe Quevauviller and K. Clive Thompson

List of Contributors

Jean Baron	CRECEP, 144, 156, av. Paul Vaillant-Couturier, Paris, F-75014, France
A.-Hakim R. Elwaer	Petroleum Research Centre, Chemistry Research Department, PO Box 6431, Tripoli, Libya
Fred S. Hauchman	US Environmental Protection Agency, Office of Research and Development (B105-01), Research Triangle Park, NC 2771, USA
Pierre Hecq	European Commission, Rue de la Loi 200, B-1049, Brussels, Belgium
Adriana Hulsmann	Kiwa Water Research, PO Box 1072, 3430 BB Nieuwegein, The Netherlands
Jennifier L. McLain	Office of Water, US Environmental Protection Agency, 1200 Pennsylvania Avenue, Washington, DC 20460, USA
Cameron W. McLeod	Department of Chemistry, Centre for Analytical Sciences Sheffield University, Sheffield, S3 7HF, UK
Philippe Quevauviller	DG Environment (BU9 3/121), European Commission, Rue de la Loi 200, Brussels, B-1049, Belgium
Franz Schmitz	Landesbetrieb Hessisches Landeslabor, Abteilung V Umwelt- und Spurenanalytik, Fachgebiet V 3 Umweltanalytik, Kurfüstenstraße 6, D-65203 Wiesbaden, Germany
Nellie Slaats	Kiwa Water Research, PO Box 1072, 3430 BB Nieuwegein, The Netherlands

K. Clive Thompson ALcontrol Laboratories, Templeborough House, Mill Close, Rotherham, South Yorkshire, S60 1BZ, UK

Theo Van den Hoven Kiwa Water Research, PO Box 1072, 3430 BB Nieuwegein, The Netherlands

1
Drinking Water Regulations

Pierre Hecq, Adriana Hulsmann, Fred S. Hauchman, Jennifer L. McLain and **Franz Schmitz**

Analytical Methods for Drinking Water: Advances in Sampling and Analysis Edited by P. Quevauviller and K. C. Thompson © 2006 John Wiley & Sons, Ltd. ISBN: 0-470-09491-5

Disclaimer: The views expressed herein are those of the authors and do not necessarily represent the views of the European Commission nor of the US Environmental Protection Agency policy.

1.1 EU DIRECTIVE ON DRINKING WATER – PAST, PRESENT AND FUTURE

1.1.1 EU Water Legislation

Water is one of the most comprehensively regulated areas of EU environmental legislation. Early European water policy began in the 1970s with the adoption of political programmes as well as legally binding legislation. As regards programmes, the First Environmental Action Programme covered the period 1973–76. Parallel with political programmes, a first wave of legislation was adopted, starting with the 1975 Surface Water Directive and culminating in the 1980 Drinking Water Directive 80/778/EEC. This initial directive was based upon the scientific and technical state of the art of 25 years ago. Since then both scientific and technological knowledge and the approach to EU legislation has changed. It was therefore necessary not only to adapt the original directive to bring it in line with the current scientific and technical progress, but also to bring it into accordance with the principle of subsidiarity by reducing the number of parameters that member states were obliged to monitor and by focusing on compliance with essential quality and health parameters.

1.1.2 The Drinking Water Directives – Revision Processes

In 1993 the commission organized a European drinking water conference in Brussels to consult all stakeholders in the supply of drinking water about the revision of the

DWD then in force. This resulted, in 1998, in the adoption and entry into force of the current DWD 98/83/EC (OJ L 330, 5.12.98). The 1998 DWD had to be transposed into national legislation 2 years after coming into force, which was at the end of the year 2000, and had to be complied with by the end of 2003 (with some exceptions for critical parameters such as lead and disinfection by products).

In the meantime the commission started preparations for the revision of the new DWD some 5 years after it came into force. This revision process is foreseen in the DWD. Exactly 10 years after the consultation of European stakeholders, the commission started to consult stakeholders on the need for revision of DWD 98/83/EC. This time 25 countries will be involved

1.1.3 Main Aspects of the Drinking Water Directives

Related Community legislation

The first generation of EU water legislation consisted of more or less isolated pieces of legislation, with little or no cross-referencing. The previous DWD 80/778/EEC only makes reference to one piece of EU legislation, namely the Council Directive on the Quality of Surface Water, intended for the abstraction of Drinking Water (75/440/EEC). The current DWD refers to a number of other directives that are related to the original directive or have interactions with that directive:

- the Plant Protection Directive (91/414/EEC) and the Biocides Directive (98/8/EC) both relevant for the pesticides parameter in the Directive and

- the Construction Products Directive (89/106/EEC), relevant for materials and appendages used in the production and distribution of drinking water.

In future revisions of the DWD, attention will be paid to an integrated approach to EU water legislation as the directive has to be brought into line with important developments such as the Water Framework Directive and the European Acceptance Scheme (under development) for materials in contact with drinking water.

Integration of EU water legislation does not only imply compliance with the requirements of various related directives but will also involve harmonization and streamlining of reporting requirements. Reporting requirements will have to address compliance and the state of, and trends in, the quality of aquatic environments.

Principles for drinking water directives

The underling principle for the previous DWD was not specified other than that it had the objective of ‘setting standards for human health protection’. The current

DWD aims to protect human health from the adverse effects of contamination of water intended for human consumption by ensuring that it is 'wholesome and clean'. This applies to all water intended for human consumption, as well as to water used in the production and marketing of food, with certain exceptions. Member states are required to monitor the quality of drinking water and to take measures to ensure that it complies with the minimum quality standards. It also lays down a number of requirements for reporting to the commission, and for making information available to the public regarding the quality of drinking water. The directive is based on a number of principles that have been laid down in the Treaty, such as the subsidiarity principle and the precautionary principle. Unlike the early Community legislation, the new Treaty of the European Union states that no Community legislation should go beyond what is necessary to achieve the objectives of the treaty. For drinking water legislation this implies that the high number of parameters in the previous directive has been reduced the better to focus on what are essential and health related parameters in the whole European Union, leaving member states free to add other parameters if they see fit. A HACCP-based directive might reduce the number of parameters even further.

Other principles of the current directive are the precautionary principle, sustainable use of water and water source protection, and of course the political compromise that goes hand in hand with the process of adoption of new legislation by the member states. If future legislation should be based on risk assessment and risk approach, the added value of such an approach should be made clear. Also such an approach should offer at least the same protection level as the current legislation in force. Other basic principles of the directive are the stand-still principle, implying that the implementation of the directive should not result in deterioration of the current level of protection offered in the member states. Also water source protection and sustainable use of water are important aspects of the directive. Also, as in all legislation, compromises are made to accommodate political aspects in the various member states. Future legislation will evidently have to be based on the principles as worded in the treaty, but after careful weighing of advantages and disadvantages of a risk analysis based approach, the principles of such an approach could easily be incorporated into the directive.

Types of water covered by the DWD

The previous DWD covered all water intended for human consumption except for natural mineral waters, medicinal waters, and water used in the food industry not affecting the final product. The current directive covers the same types of waters and has the same exceptions. It also makes it possible for member states to exempt other types of water from the directive, such as hot tap water, second grade water for non-ingestive uses and supplies of less than 10 m^3/day. As yet it is not known if there is a need to change the coverage of the DWD in future revisions of the directive.

Parameters and parametric values

The previous DWD listed more than 62 parameters often together with parametric values such as MACs (maximum allowable concentration), guideline values and minimum levels. Parameters included organoleptic, physico-chemical parameters, undesirable substances, toxic substances, microbiological parameters and minimum requirements for water that had been subject to water conditioning processes to remove hardness. Not all parameters actually had a parametric value in the directive and also no mention was made of the scientific justification for the parameters and the values in the directive. Substances that were used in the preparation of drinking water should remain in the water at values below the parametric value for these substances. One of the main reasons for the revision of the old directive was to restrict the number of parameters to include only essential and health related parameters that are of importance in the many countries of the European Union. It is then left to member states on the basis of the subsidiarity principle to add parameters or to set stricter values as and where necessary but with no breaching the treaty with respect to the rules of fair trade within the EU. The number of parameters is restricted to a total of 48 (microbiological, chemical and indicator) parameters. All parameters that are included in the directive have a parametric value or mention of the fact that water 'should be acceptable to consumers and no abnormal change' should occur. All parametric values are mandatory and guide level values no longer exist in the directive. For future revisions of the DWD discussions could result in new and additional parameters or in even fewer parameters. New parameters might, for example, be endocrine disrupting chemicals, pharmaceuticals, protozoa such as *Giardia* spp. and *Cryptosporidium* spp. or *Legionella* spp. In a risk-analysis based approach it might also be possible that one parameter may have more than one parametric value in various parts of the whole water production and supply process.

Parameters in DWD 98/83/EC

In this DWD a balance is struck between microbiological and chemical risks. Disinfection of drinking water carries the risk of contamination by formation of products that are harmful to human beings, such as trihalomethanes and bromate. However, disinfection reduces the risk of exposure to pathogenic bacteria in the water. Water quality is more than the 48 parameters listed in the current directive. Some parameters that might cause a threat to human health are not yet known. Therefore the DWD has to reinforce the precautionary principle, an important article (Article 4(1)a), which states that water intended for human consumption should be 'wholesome and clean'. Article 10 of the DWD ensures that chemicals used in the preparation of drinking water should not remain in the final product in concentrations higher than absolutely necessary. Another important aspect of Article 10 is the reference to the Construction Products Directive on materials in contact with drinking water during

its distribution, in order to avoid an adverse effect on the quality of drinking water by pipe materials, for example.

Basis of parametric values

In setting the parametric values for the various parameters, both short term/acute effects and long term chronic effects have been taken into account as and where appropriate. Basic principles are that the quality of the water should be such that consumers can drink and use water for domestic purposes for a lifetime without the risk of adverse health effects. Also special attention is paid to the protection of vulnerable groups such as children and pregnant women, for instance in setting the values for lead, nitrate and nitrite (babies). WHO guideline values for drinking water, adopted in 1992, were used as a basis for setting parametric values in the DWD, wherever there was a health-based guideline value available. For some parameters a different approach was used, and for others advice was asked of the CSTEE (Scientific Advisory Committee). Parameters in the last category were lead, PAH, pesticides, tri- and tetra-, copper and boron.

Microbiological parameters

The parametric values for the relevant specified microbiological parameters are zero as any positive result indicates the likely presence of pathogenic microorganisms and calls for an immediate response.

Carcinogenic parameters

For genotoxic carcinogens there is normally no threshold below which there is no risk to human health. The WHO applies a criterion for individual carcinogens that implies that there should be no more than one excess cancer in a population of 10^5 resulting from a lifetime's exposure. In the DWD a stricter criterion was used, which implies that there should be no more than one excess cancer in a population of 10^6 resulting from a lifetime's exposure.

Other considerations

A very practical consideration in setting parametric values is the availability of fit-for-purpose analysis methods at the required detection level. For three parameters in the DWD it was, at the time of adoption, not possible to detect the substances at a level that would sufficiently protect human health. For these three parameters, epichlorohydrin, acrylamide and vinyl chloride, a parametric value was adopted

that was below the then achievable limit of detection, and for these parameters it was decided to regulate levels in drinking water through product specifications. A second principle for setting parametric values is the availability of treatment methods to ensure that the required removal of the substances could be achieved with the available treatment techniques. Finally, a balance was struck between the risk to human health from the consumption of water not meeting the high standards foreseen in the DWD and the risk from interruption of the water supply (sometimes applying parametric values not as strict as that corresponding to the one in a million criterion).

Sampling and monitoring

The previous DWD 80/778/EEC defines minimum monitoring requirements with a sampling and analysis frequency that is related to the amount of water supplied. A distinction is made between current monitoring, periodic monitoring and occasional monitoring. The current DWD 98/83/EC uses a similar approach where minimum monitoring effort is defined in relation to the amount of water supplied. A regular check of the water quality is defined for some key parameters in so-called check monitoring, and a more comprehensive check of the water quality including all other parameters is carried out with a much lower frequency in so-called audit monitoring. The main difference between both directives is the fact that under the current DWD sampling and monitoring is carried out at the consumer's tap unless it relates to parameters that do not change between the production plant and the tap. Sampling and monitoring under the DWD is, in principle, a check at the last minute and is, in principle, always too late. In the case of water not complying, it has already been supplied to the customer and been consumed. A risk-assessment and risk-management based approach could well cause a major change in sampling and monitoring strategies for drinking water. Moving the place of check and control further back in the production chain from raw water source to tap may be beneficial for some parameters.

Quality control and assurance

Quality control in the 80/778/EEC DWD was restricted to the mention of analytical reference methods. The current DWD goes much further by making ISO/CEN methods compulsory and defining performance criteria for (mostly) chemico-physical parameters. Furthermore, member states need to have some QC/QA system in place in the approved laboratories for drinking water analyses. At the time of adoption of the DWD it was not judged possible to apply an accreditation system for all member states, but it is expected that this will be an additional requirement in the near future.

As future regulation might well be based on risk analysis and approach, the QC/QA system is of vital importance not only to control process performance but also to validate and guarantee the quality of drinking water at the tap.

1.1.4 Revision of the DWD and WHO Guidelines

WHO has adopted the HACCP based approach for drinking water in the so called 'water safety plans'. The European Commission is currently considering whether it would be appropriate to follow this concept in the revision of the DWD.

Issues that will be addressed by the experts in the revision will include such basic questions as how can the underlying principles of the treaty (and the DWD) be maintained and safeguarded in a risk assessment approach:

- subsidiarity principle;
- stand-still principle;
- precautionary principle.

The main question is, of course, how can the same or even higher level of protection of European citizens continue to be guaranteed.

1.1.5 Conclusions

The EU regulation on drinking water has contributed significantly to the supply of safe and wholesome drinking water to European citizens. The current DWD 98/83/EC even improves on that by setting requirements for the quality of drinking water at the consumer's tap. Council directives on drinking water are to a large extent based on WHO guidelines and it is therefore logical that any developments in these guidelines will have to be considered in the revision of the DWD. It is expected that the underlying principles of the current DWD will be further strengthened by a HACCP-like approach. When applied properly and consistently, the added value of a risk-assessment based approach, together with the existing framework of the directive, will be a powerful tool for addressing new and, as yet, partly unknown threats to drinking water such as, for instance, pharmaceuticals, endocrine disrupting chemicals, algal toxins and microorganisms such as *Cryptosporidium*, *Giardia* and viruses. Extending the control of water quality from the final product at the tap to the whole production process will, when accompanied by adequate information to the public, boost the confidence of European consumers in the safety and wholesomeness of their drinking water. Close cooperation between the European Commission and WHO is a prerequisite for achieving this target.

1.2 DRINKING WATER REGULATIONS IN THE UNITED STATES

1.2.1 Introduction

Public water systems in the United States provide high quality drinking water to millions of Americans each day. The application of the multi-barrier concept – that is, selecting and protecting the best available source, using water treatment to control contaminants, and preventing water quality deterioration in the distribution system – has virtually eliminated waterborne diseases of the past such as typhoid and cholera. Nevertheless, some challenges to the safety of the water supply remain. Waterborne disease outbreaks caused by pathogenic microorganisms and toxic chemicals continue to be reported. Contamination of surface and groundwater supplies with various natural and man-made substances may pose either acute or chronic risks if treatment is inadequate. Post-treatment contamination of the distribution system may also pose public health risks. Special groups, such as infants or those with weakened immune systems, may be particularly sensitive to the effects of certain waterborne pathogens and chemicals.

In response to these concerns, the US has enacted strong legislation to ensure the safety of the nation's drinking water supply. The Safe Drinking Water Act (SDWA) authorizes the US Environmental Protection Agency (EPA) to establish national health-based standards that reduce public exposure to microbiological, chemical and radiological contaminants of concern. These federal standards currently apply to approximately 170 000 public water systems throughout the US.[1]

1.2.2 History of the Safe Drinking Water Act

The first national standards for drinking water quality were established by the US Public Health Service in 1914. These standards addressed the bacteriological quality of drinking water and applied only to interstate carriers such as ships and trains. The Public Health Service revised and expanded these standards in 1925, 1946 and 1962, with the latter including regulations for 28 substances. Throughout the 1960s and early 1970s, both the public and Congress became increasingly concerned about the contamination of water supplies by agricultural and industrial chemicals. Surveys indicated that many treatment facilities across the country had major deficiencies. The heightened public awareness about this and other environmental problems led the US government to pass a number of important environmental and public health laws. One of these laws, the Safe Drinking Water Act (SDWA), was passed in 1974 and subsequently amended in 1986 and 1996.

[1] Public water systems regulated by EPA may be publicly- or privately-owned, and must serve at least 25 people or 15 service connections for at least 60 days per year. Bottled water is regulated by the US Food and Drug Administration.

1.2.3 Development of Regulations

Overview

The regulatory development process under SDWA begins with an evaluation by EPA of the available science on the health effects and occurrence of a drinking water contaminant. If a contaminant is considered to pose a potential public health risk, EPA conducts a more extensive analysis that involves a detailed review of health effects, occurrence, treatment options, available analytical methods, costs, and benefits. Outside stakeholders, representing groups such as the water industry, environmental and community associations, State regulators and public health organizations, are involved throughout the regulatory development process. EPA then publishes a proposed regulation and solicits public comments. A final regulation is published after considering public comments and any new information that may become available.

Drinking water standards

Each regulated contaminant has a non-enforceable health goal, or maximum contaminant level goal (MCLG), and an enforceable limit, or maximum contaminant level (MCL). An MCLG is established at the level of a contaminant in drinking water for which there is no known or expected health risk. The MCLG is set at zero for microbial pathogens as well as for chemicals that may cause cancer through a nonthreshold mechanism of action. If there is evidence that a carcinogen may exhibit a threshold below which cancer may not occur, the MCLG is set at a level above zero that is considered to pose no risk. For chemicals that are of concern due to the potential for adverse health effects other than cancer, the MCLG is based on the calculation of a reference dose (RfD). The RfD is an estimate of the amount of a chemical that a person can be exposed to on a daily basis that is not anticipated to cause adverse health effects over a person's lifetime. The reference dose is converted into a drinking water exposure level (DWEL) by incorporating default exposure assumptions for body weight (70 kg) and for average daily consumption of drinking water (2 l per day). The DWEL is then used to calculate an MCLG by adjusting it to account for sources of exposure other than drinking water, such as food and air. An MCLG is designed to be protective of sensitive sub-populations that may be at greater risk than the general population (e.g., infants, the elderly, those with compromised immune systems). In addition, an MCLG may be set at levels that are not measurable or quantifiable by currently available analytical methods.

SWDA requires the EPA to promulgate National Primary Drinking Water Regulations (NPDWRs), which specify enforceable maximum contaminant levels (MCLs) or treatment techniques for drinking water contaminants. An MCL is established at a level that is as close to the MCLG as is technically and economically feasible. A treatment technique may be set instead of an MCL if the available analytical methods

are not adequate. NPDWRs contain specific criteria and procedures, including requirements for water monitoring, analysis and quality control, to ensure that the drinking water system is in compliance with the MCL. EPA has established MCLs or treatment techniques for a wide range of microorganisms, disinfectants, disinfection byproducts, inorganic and organic chemicals, and radionuclides (EPA, 2004a).

EPA also sets National Secondary Drinking Water Regulations for contaminants that affect the aesthetic (e.g., taste, color or odor), cosmetic (e.g., skin or tooth discoloration) or technical (e.g., corrosivity or scaling) qualities of drinking water. These non-enforceable guidelines include secondary MCLs and recommendations for monitoring (EPA, 2004b).

1.2.4 Highlights of the Safe Drinking Water Act

Implementation of the 1986 Amendments to SDWA led to the development of a number of important rules, including the Total Coliform Rule, the Surface Water Treatment Rule, the Lead and Copper Rule, and regulations for a large number of chemicals of public health concern. All public water systems using surface water sources were required to disinfect and provide specific levels of treatment for microbial pathogens; most systems were required to filter their water. In addition, the 'best available technology' was specified for the treatment of contaminants for which an MCL was established.

The 1996 Amendments greatly enhanced the previous regulatory approach in many respects. In addition to reinforcing the use of sound science in fulfilling the requirements of the Act, a cornerstone of the 1996 Amendments is the fundamental requirement for EPA to use a risk-based standard setting process. The amendments place a strong emphasis on protecting source waters, improving the regulatory process, and conducting research on contaminants of concern. Provisions address the special needs of small water systems, and include requirements for making water quality information available to consumers, conducting health risk reduction benefit analyses, and helping states meet water system infrastructure needs. The EPA is required to develop rules to achieve the goal of providing protection from microbial pathogens while simultaneously ensuring decreasing health risks to the population from disinfection byproducts. A brief discussion of some of the major regulatory and nonregulatory provisions of SDWA is found below.

Regulated contaminants

Six-year review of existing regulations The EPA is required by the 1996 SDWA Amendments to review each NPDWR at least once every 6 years. Revisions must maintain or increase public health protection. In consultation with stakeholders, the EPA developed a systematic approach for the review of the NPDWRs. This protocol was applied to the Agency's initial Six-Year Review of most of the NPDWRs

published prior to the 1996 Amendments. In 2003, EPA published final decisions to not revise 68 chemical NPDWRs and to revise the Total Coliform Rule (TCR). The schedule for reviewing NPDWRs established after 1996 will be based on the respective promulgation dates of these rules (EPA, 2004a, c).

The TCR, published by EPA in 1989, requires all public water systems to monitor for the presence of coliforms (measured as 'total coliforms') in their distribution systems. Coliforms serve as indicators of many enteric pathogens, and are therefore useful in determining the vulnerability of a system to fecal contamination. In reviewing microbial risks with a federal advisory committee, EPA determined that the available data on distribution system risks warranted further analysis. Potential revisions being considered may lead to the establishment of requirements to address the quality of finished water in distribution systems (EPA, 2004d).

Microbial/disinfection byproduct rules Minimizing the potential health risks associated with exposure to disinfection byproducts (DBPs) without compromising the safety of drinking water from a microbiological perspective poses a major challenge for drinking water providers. In keeping with a phased Microbial/Disinfection Byproduct strategy agreed to by stakeholders and affirmed by the 1996 SDWA Amendments, the EPA has proposed or finalized a number of rules that address both microbial and DBP concerns (EPA, 2004e). The Stage 1 DBP Rule, finalized in 1998, established Maximum Residual Disinfectant Levels (MRDLs) and Goals (MRDLGs) for three disinfectants; MCLGs and MCLs for trihalomethanes, haloacetic acids, chlorite and bromate; and a treatment technique for removal of DBP precursor material. A new Stage 2 DBP Rule, which will be promulgated in 2005, will provide additional public health protection from the potentially harmful effects of DBPs. The proposed rule retains the Stage 1 MCLs but includes revised requirements for collecting monitoring data and calculating compliance. The rule also requires an initial distribution system evaluation that targets the highest risks by identifying compliance sites with the highest DBP occurrence levels in the distribution system.

A series of microbial rules is being developed and implemented concurrently with the DBP rules. The first of these rules, the Interim Enhanced Surface Water Treatment Rule (IESWTR), was finalized in 1998. Key provisions include treatment requirements for *Cryptosporidium* for filtered water systems, tightened turbidity standards, and inclusion of *Cryptosporidium* in the watershed control requirements for unfiltered public water systems. In 2002, EPA finalized the Long-Term 1 Enhanced Surface Water Treatment Rule (LT1ESWTR). This rule extends the provisions of the IESWTR to cover all system sizes, particularly those serving $<10\,000$ individuals. The LT1ESWTR improves control of *Cryptosporidium* in drinking water and addresses risk trade-offs with DBPs. The next generation of surface water treatment rule, the LT2ESWTR, coincides with the proposal and promulgation of the Stage 2 DBP Rule. The LT2ESWTR will strengthen protection against *Cryptosporidium* in the highest risk systems.

The Ground Water Rule (GWR) is a targeted strategy to identify ground water systems at high risk for fecal contamination. The proposed rule establishes a multiple barrier approach to identify and provide corrective measures for public ground water systems at risk of fecal contamination. The GWR will be issued as a final regulation in 2006.

Unregulated contaminants

The 1996 Amendments include a risk-based contaminant selection and decision making process for unregulated contaminants. The EPA must decide whether or not to regulate at least five contaminants every 5 years, based on a consideration of the following three criteria: (i) that the contaminant adversely affects human health; (ii) that it is known or substantially likely to occur in public water systems with a frequency and at levels of public health concern; and (iii) that regulation of the contaminant provides a meaningful opportunity for health risk reduction.

Every 5 years, the EPA is required to develop a list of unregulated microbiological and chemical contaminants that may be regulated by the EPA at some future date (EPA, 2004f). The list, referred to as the Contaminant Candidate List (CCL), was first published by EPA in 1997 and finalized in 1998 after extensive consultation with stakeholders. In establishing the CCL, EPA divided the contaminants into three major categories: (i) a Regulatory Determination Priorities Category, with contaminants that have enough data to determine whether a regulation is necessary; (ii) a Research Priorities Category, which contains contaminants with additional research needs in the areas of health effects, treatment, and/or analytical methods; and (iii) an Occurrence Priorities Category, with contaminants for which additional occurrence data are needed. The 1998 CCL included 50 chemicals and 10 microbial pathogens, most of which were in the Research and Occurrence Priorities Categories.

In 2003, the EPA announced its determination that no regulatory action was appropriate or necessary for nine contaminants on the first CCL. These contaminants included aldrin, dieldrin, hexachlorobutadiene, manganese, metribuzin, naphthalene, sodium, sulfate, and *Acanthamoeba* (for which guidance was developed). A second CCL, issued in 2005 (EPA, 2005), included all the contaminants from the previous CCL for which a regulatory determination was not made. The EPA is developing a more rigorous process for selecting contaminants for future CCLs, using guidance from the National Academy of Sciences (2001) and the National Drinking Water Advisory Council (2004).

National Occurrence Data Base and the Unregulated Contaminant Monitoring Rule

SDWA has provisions that provide for the collection, organization and sharing of occurrence data on contaminants of potential concern. The National Drinking Water

Contaminant Data Base (NCOD) is a website repository of water sample analytical data on both regulated and unregulated contaminants in public water systems (EPA, 2004g). These data are used to support listing and regulatory determinations on contaminants for which regulations do not currently exist, as well as reviews of existing regulations and monitoring requirements. Under the requirements of the Unregulated Contaminant Monitoring Rule (UCMR), EPA is required to issue a list every 5 years of up to 30 unregulated microbiological, chemical and radiological contaminants for which monitoring is required by water utilities across the country (EPA, 2004h). Depending upon the availability of adequate analytical methods and current contaminant occurrence data, UCMR contaminants may be subjected to the full assessment monitoring, a screening survey, or a pre-screen testing. This rule has important implications for the development of new or improved analytical detection methods for contaminants of potential public health concern.

Prevention approaches

The 1996 amendments include an important new emphasis on preventing contamination problems through source water protection and enhanced water system management. Source water protection is an ongoing process that includes conducting assessments to understand the vulnerabilities of the source to contaminants, monitoring to detect contamination as early as possible, protecting sources using best management practices, and planning for quick response when contamination occurs. The central responsibility for source water assessments, as well as designing and implementing prevention programs, resides with the states. The states also have the responsibility for building the capacity of local water systems to improve system operations and avoid contamination problems.

The national Wellhead Protection Program, established under the 1986 amendments, is a pollution prevention and management program used to protect underground sources of drinking water. States may use the funds from the SDWA-authorized Drinking Water State Revolving Fund to support a mixture of source water-related local assistance activities. Source water protection activities are also supported by other statutory authorities, particularly the Clean Water Act (CWA), the Resource Conservation and Recovery Act (RCRA), the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA).

1.2.5 Implementation of Regulations

Once the EPA publishes a final regulation, systems usually have 3 years before they must be in compliance. The states are typically responsible for the implementation and enforcement of standards established by the federal government. The EPA provides oversight, funding and technical assistance to help states administer their

programs. Compliance with the standards is determined through the collection, testing and reporting of samples taken from water systems at designated intervals and locations. The use of EPA-approved analytical methods and certified laboratories (EPA, 2004i) is required for compliance monitoring.

In cases of non-compliance, different types of violations may occur: (i) MCL violations; (ii) treatment technique violations; or (iii) monitoring and reporting violations. Varying levels of public notification are required depending on the type of violation, and corrective action must be taken to remedy the situation. EPA works with the states to enforce drinking water standards.

1.2.6 Conclusions

The US has achieved considerable success in ensuring the safety of the public drinking water supply, particularly since SDWA was first passed over 30 years ago. This has been accomplished through the combined efforts of drinking water and health professionals at the federal, state and local levels. Source water protection programs have been implemented, disinfection of public water supplies has become widespread, and regulations to reduce public exposure to a wide range of contaminants have been established. Sensitive analytical detection methods have made it possible to detect a wider range of microbes and chemicals at increasingly lower environmental levels, and improved treatment technologies have become available. In addition, the public has become much more informed and involved in decisions about the safety of their water supply. Effective implementation of SDWA requirements and the cooperation of the drinking water community will continue to be necessary in the coming years in order to meet the challenges posed by new concerns about the quality and quantity of the nation's drinking water supply.

1.3 STANDARDIZATION

1.3.1 Introduction

Legislative directives on the quality of drinking water call for wholesome, clean, and safe water. The European directive, as an example, specifies that the analytical methods used for drinking water should ensure that the results obtained are reliable and comparable (Council Directive 98/83/EC, 1998). Possible risks for the consumer of drinking water from various toxic and health concerns shall be investigated and monitored, e.g. chemical or microbiological contaminants from natural sources or pollutants from material being in contact with drinking water. The result of these investigations is a list of contaminants including an upper limiting value for each of the parameters. Drinking water directives, such as that from the European Union (EU) (Council Directive 98/83/EC, 1998), publish such lists.

1.3.2 Requirements to be Met by Laboratories and Analytical Methods

An effective control of drinking water quality generally is based on data obtained from samples analysed in laboratories.

Regulators, clients, and consumers expect to receive a 'true' result from the laboratory. In order to avoid a semantic discussion about 'what is the true result?', legislators generally define quality requirements to be met by the analytical method and by the laboratory. The minimum requirements to be met by the analytical methods used, according to the European directive (Council Directive 98/83/EC, 1998), shall be capable of measuring concentrations equal to the parametric value with a specified trueness, precision, and limit of detection.

Laboratories shall operate a system of analytical quality control that is subject to checking from time to time by a person who is not under the control of the laboratory and who is approved by the competent authority for that purpose (Council Directive 98/83/EC, 1998). A suitable direction for such a competence check is available (EN/ISO/IEC 17025, 2005). Laboratories qualified for drinking water analyses should fulfill the requirements for an accreditation procedure preferably according to EN/ISO/IEC 17025 (2005).

The laboratories need validated methods for performing a variety of required characteristics, e.g. robust against possible matrix interferences or matrix changes (e.g., hardness), specific and selective for the contaminant of interest, suitable working range, applicable for the control of a maximum contaminant level. Additional desirable characteristics are that the methods should, for example, allow simplified sample preparation, rapid analyses, economical benefits, avoidance of hazardous reagents (e.g., certain solvents), robust apparatus, compatible with the requirements of an analytical quality control (AQC) system.

Approved and validated methods appropriate for drinking water analyses are generally standardized methods. These methods have normally been developed especially for drinking water analyses. During the standardization project the draft standard methods have to go through a validation procedure, including checks for trueness, precision, recovery, and finally an interlaboratory trial before they are published as a standard method.

1.3.3 Standardization in CEN TC 230 Water Analysis and ISO TC 147 Water Quality

General

Standardization is one of the tools used to organize the technical world. Standardization has become an integral component of the economic, social, and legal systems.

International standards from the International Standards Organization (ISO) and European standards (EN) from the European Standardisation Organization (CEN) can remove trade barriers and promote business across national frontiers. Standardization is based on consensus, on scientific findings and on technical progress, and one has to bear in mind the economic consequences (DIN, 1998).

Standardization in CEN and ISO has to be well-founded. Before the work on a new standardization project can start the applicant country has to explain the need and reason for a new standard (see Section 1.3.4 stage 2).

The philosophy of setting standards in CEN and ISO on the one hand and the US Environmental Protection Agency (EPA) on the other hand is different. CEN and ISO prefer documents that do not specify trademarks or equipment produced by a single manufacturer (monopolies), whenever possible (ISO/IEC, 2001) (see Section 1.3.6).

Standard methods (e.g., from ISO, CEN, and EPA) can be adopted as recommendations on a voluntary basis by any laboratory around the world. Governments can decide to incorporate existing standards into their national standards. European standard methods are essential for the national standards politics in Europe: generally, CEN standards shall replace any of the national standard methods within the European member bodies in order to harmonize analytical standard methods (ISO/TC 147, 2003).

Standardization on a European level is the responsibility of CEN. Standardization on an international level is the responsibility of ISO. Today, some 120 national standardization bodies cooperate in activities that aim to stimulate cooperation in the scientific, technical, and economic spheres across national frontiers. Generally, European standards (EN) are based on ISO standards (DIN, 1998).

CEN and ISO standards are elaborated in technical committees (TC) installed for a particular field of action. ISO/TC 147 'Water Quality', founded in 1971, is responsible for the standardization of water analysis methods. The corresponding European committee is CEN/TC 230 'Water Analysis', founded in 1990 (ISO/TC 147, 2003).

Vienna Agreement

Today, CEN and ISO cooperate according to the so-called Vienna Agreement of 1991 in order to save resources and to avoid duplication of work or contradictory standard methods in CEN and ISO. Both organizations agreed on basic principles, for example, on synchronized approval procedures or simultaneous publication. Standardization projects started in ISO can be transferred to CEN, if necessary, and vice versa. The transfer process can be started either by the so-called unique acceptance procedure (UAP, see Section 1.3.5) on a finalized ISO or CEN standard or by the parallel voting procedure (PVP, see Section 1.3.5) on a document qualified for an enquiry process (ISO/CEN, 2001).

Today, most of the standards on water quality are elaborated in ISO/TC 147 before they are transferred to CEN (ISO/TC 147, 2003). Section 1.3.4 describes the

procedural steps for the standards elaboration in ISO because they need to meet the requirements for approval in CEN, too.

1.3.4 Development of Standards in ISO/TC 147

General

Today, ISO/TC 147 is subdivided into five subcommittees (SC) working on:

- SC 1 terminology;
- SC 2 physical, chemical, and biochemical methods;
- SC 4 microbiological methods;
- SC 5 biological methods;
- SC 6 sampling.

Each of the subcommittees has set up several working groups (WG). Usually, work items will be allocated to a working group.

National member bodies decide which of the committees they want to support. Member bodies are asked to state their opinion of a distinct field of work by commentaries and by voting on items.

ISO standard methods are developed according to the ISO/IEC Directives, Part 1 (ISO/IEC, 1995). Each of the development stages ends in a decision about whether the project should be continued, postponed, or withdrawn. The ISO Central Secretariat (ISO/CS) in Geneva, Switzerland is responsible for all of the formal aspects (e.g., controlling the standardization process, observance of deadlines for voting processes, distribution of all documents, etc.). The working group is responsible for the technical and editorial work and shall report to the subcommittee (SC) and the technical committee. In ISO/TC 147 Committees and working groups generally meet every 18 months.

Development of standards follows a seven-step procedure (ISO/IEC, 1995). See Table 1.1 for the principles of the ISO standardization process.

Stage 1 – Preliminary

The preliminary stage is applied to a new project. The introduction of a new item requires a simple majority vote of the respective committee member bodies. This stage has no target dates to be considered. The advantage of working without time pressure can be used to prepare a carefully thought out initial draft for the proposal stage.

Table 1.1 Standards development according to ISO/IEC Directives

Stage	Business	Requirements/Comments
1 Preliminary stage	ISO member applies for a new standard proposal	Give purpose and justification for the need of new method
		Approval by a simple majority
2 Proposal stage	Written ballot on a new work item proposal (NP) by members within three months necessary	Approval by a simple majority of member bodies *and* a minimum of five members shall participate actively in the project
3 Preparatory stage	Preparation of a working draft (WD)	Elaboration of a WD for circulation to the members
4 Committee stage	Preparation of a committee draft (CD) and its circulation to all member bodies to comment on it within 3 to 6 months	Consensus, this means a two-thirds majority of member bodies voting on the CD should be in agreement
5 Enquiry stage	Preparation of a Draft International Standard (DIS) and its circulation. Voting period: 5 months. A positive vote may contain minor technical comments	Approval of more than 66.7 % members necessary *and* a maximum of 25 % or fewer disapprovals allowed
6 Approval stage	Preparation of a Final Draft International Standard (FDIS) and its circulation. Voting period: 2 months	Approval of more than 66.7 % members necessary *and* a maximum of 25 % or fewer disapprovals allowed
7 Publication stage	Publication of an ISO standard method	The method is valid for 5 years
Review of a standard	Confirmation of the standard method every 5 years	The method is valid for another 5-year period
Withdrawal of standard	Withdrawal of a standard method, if the standard did not pass Stage 7 successfully or a confirmation at the revision date was not permitted	The method will be deleted from the standards project list

Stage 2 – Proposal

The proposal stage is used for a new standard, and for any amendment and/or revision of an existing standard. A new work item proposal (NP) may be made to the respective committee by, for example, a national body, the secretariat of that technical committee or subcommittee, or an organization in liaison. The applicant has to indicate, among other things, the subject of the proposed item, clarification of the scope and, if necessary, what is excluded, plus specific aims and reasons for a new standard.

Where possible, a draft (e.g., elaborated in the preliminary stage) should be sent out with the new work item proposal, but as a minimum an outline should be attached for the voting procedure. Votes shall be returned within 3 months, and comments on the new proposal are encouraged.

Approval of the new proposal requires a simple majority of the committee members voting on the proposal and at least five member countries willing to participate actively in the project.

Stage 3 – Preparatory

The approved new project will be allocated to a working group. Experts nominated for the participation in the project shall agree on a working group member to act as convenor. The working group prepares a working draft (WD). The working draft should be available within 6 months. The convenor of the working group is responsible for the progress, the editorial work, and the preparation of the working draft according to the target dates.

At the end of this stage the working draft is circulated among the members of the technical committee or subcommittee as a first committee draft (CD).

Stage 4 – Committee

The committee stage is used to circulate the first committee draft to all member bodies for consideration. Votes and comments shall be returned to ISO within 3 months. ISO shall circulate the result of the ballot and a compilation of comments to all member bodies not later than 4 weeks after the closing date for voting. The secretariat shall also indicate its proposal on how to proceed with the project.

Formal approval of the Committee Draft requires a two-thirds majority of the member bodies voting, but ISO sets a high value on the consensus principle.

Following the consensus principle in ISO, every attempt shall be made to resolve all of the negative votes and comments received. That may require the preparation and circulation of a second or subsequent versions of the committee draft until consensus has been reached or a decision to postpone or withdraw the project has been made. When the approval requirements have been met, an enquiry draft can be circulated. Ideally, the period between Stage 4 and Stage 5 should be used to organize and evaluate an interlaboratory trial (see Section 1.3.6). The performance characteristics obtained should be sent out with the proposal for the enquiry draft.

Stage 5 – Enquiry

At the enquiry stage the Draft International Standard (DIS, enquiry draft) shall be available in English and French for circulation to the national member bodies. Votes

and comments shall be returned to ISO within 5 months. ISO shall circulate the following documentation:

- result of the ballot;
- compilation of comments received;
- action taken on the comments,

to the national bodies not later than 3 months after the closing date for voting. The secretariat shall also indicate its proposal for proceeding with the project.

Approval of the enquiry draft requires a two-thirds majority of the member bodies voting in favour and a total number of negative votes of not more than 25 % (*Note*: negative votes without a statement about substantial reasons for the disagreement and abstentions are excluded from the total number of votes).

Comments received after the set voting deadline should be considered at the revision phase of the standard method.

The consensus principles remain valid at the enquiry stage, too. When the approval requirements have not met the enquiry draft, comments shall be discussed at a meeting of the committees (TC 147, SC 2) or of the working group, or a revised enquiry draft for voting on it, or a revised committee draft for comments shall be prepared and circulated.

When the approval requirements have been met, the enquiry draft can be forwarded for the preparation as a Final Draft International Standard (FDIS).

Stage 6 – Approval

At the approval stage the Final Draft International Standard (FDIS) shall be distributed within 3 months to all national bodies for a vote within 2 months. All negative votes shall state the technical reasons for disagreement.

Approval requirements for the FDIS are identical to those at the enquiry stage (see above).

If the FDIS fails the approval requirements, the draft shall be referred back to the technical committee or subcommittee and comments shall be discussed at the next meeting. Alternatively a revised enquiry draft for voting on it or a revised committee draft for comments shall be prepared and circulated.

If the FDIS meets the approval requirements, the FDIS can be forwarded to the publication stage.

Stage 7 – Publication

The publication stage ends with the publication of the international standard.

Five-year revision

Standards are valid for 5 years. After that period a decision shall be made to confirm the standard for a further 5 years, to revise it, or to delete it from the working programme.

Withdrawal of standards

Methods shall be deleted from the standards system if they do not pass the approval stage (see above) successfully, or a confirmation after 5 years is refused, or a replacement of an existing standard by a new one takes place.

1.3.5 Special Standards Development Procedures

Some alternative development procedures, within the requirements defined by ISO or CEN, may be applied. Alternative procedures can be beneficial for a standardization organization deciding to adopt an existing document. These alternative procedures offer the following advantages:

- resources can be saved;
- the duplication of work can be avoided;
- the speed of standards elaboration can be increased;
- consensus need to be established only once (ISO/CEN, 2001).

Fast-track procedure

This procedure may be applied if a standard method, developed by another organization is available and appropriate for a ISO standardization project. A standard method submitted directly for approval as an enquiry draft (DIS, Stage 5, see above) starts on the proposal stage (Stage 2 above). After the approval of the project it can be forwarded directly to the enquiry stage (Stage 5 above) without passing through the preparatory stage and committee stage (above), thus speeding up the development process (ISO/IEC, 1995).

Transfer of standard methods according to the Vienna Agreement

The cooperation between ISO and CEN follows the Vienna Agreement (ISO/CEN, 2001), see Section 1.3.3. Standards can be transferred to the other organization either

by the unique acceptance procedure (UAP, see section below) or by the parallel voting procedure (PVP, see section below).

Unique acceptance procedure (UAP) The organization (CEN or ISO) that wants to adopt an available standard method from the other organization submits it to its own adoption, voting, and publication procedures. The approved standard to be transferred will be balloted at the enquiry stage of the adopting organization (ISO/DIS or CEN enquiry, respectively). After the positive vote the adopted document can be finalized and published.

The technical content of the publication of the adopted standard should be identical with that of the original publication. Any intended technical alterations or changes shall be discussed and resolved with the secretariat of the developing organization in order to find a satisfactory solution. Ideally, the original standard should be revised according to the PVP (below) if a consensus about the intended changes cannot be reached and the adopting organization decides to insist on the changes. If this is not possible, the amended standard shall include information and reasons for the alteration of the original document (ISO, 2004).

Parallel voting procedure (PVP) This procedure is suitable for transferring projects already started. Once the decision has been made about a CEN or ISO project leadership, the responsible committee drafts a document according to the procedures of the leading organization. The responsible secretariats of CEN and ISO shall ensure the synchronization of the ISO/DIS–CEN enquiry for parallel voting. After a positive vote in CEN and ISO, the adopted document can be finalized and published. Otherwise consultations between CEN and ISO are necessary in order either to resolve the negative votes responsible for the disagreement or to proceed in accordance with the own rules of the respective organization (ISO, 2004).

1.3.6 Drafting of Standards

Besides formal aspects of standardization, analytical standard methods have to follow a general structure with several obligatory technical instructions in the normative body of the standard. The ISO Directives, Part 2 (ISO/IEC, 2001) give advice for the structure of ISO standards. Standard developers can gain supplementary information from a model manuscript (ISO, 1998a). See Table 1.2 for an example of the structure of a EN ISO standard method.

This concept ensures a strict definition of the application range of the standard to be applied. In addition, informative annexes may be presented in order to give further examples and information to the user. The normative part of an analytical standard method in CEN and ISO includes at least the clauses listed below (ISO/IEC, 2001; ISO, 1998). Additional clauses, such as specific definitions or a list of minimum requirements needed, may be added to the standard, if relevant.

Table 1.2 Structure of EN/ISO 15061 (2001). EN/ISO 15061 Water quality – Determination of dissolved bromate: Method by liquid chromatography of ions

Foreword
Introduction
1 Scope
2 Normative references
3 Interferences
4 Principle
5 Essential minimum requirements
6 Reagents
7 Apparatus
8 Quality requirements for the separator column
9 Sampling and sample pretreatment
10 Procedure
11 Calculation
12 Expression of results
13 Test report
Annex A (informative) Eluents
Annex B (informative) Regeneration solutions
Annex C (informative) Example of column switching technique
Annex D (informative) Interlaboratory trial
Annex E (informative) Checked interferences
Bibliography

Title

The title shall be concise and represent the parameter (sometimes also the analytical technique and matrix, if relevant) treated in the standard (ISO, 1998a). The user of the standard shall be aware that the method is strictly limited to the mentioned sample matrices and any analytical result based on an extension or alteration of the standard method in the user's laboratory cannot refer to the standard method.

Foreword

A foreword shall appear in each standard. It gives the designation and name of the technical committee and subcommittee that prepared the standard (ISO, 1998a).

Introduction

The introduction is an optional element containing commentary about the technical content of the standard or background information (ISO/IEC, 2001).

Scope

The scope specifies briefly the applicability (e.g., parameter to be determined, working range to be applied, appropriate sample matrix types) and the limitation of the method (ISO, 1998a). Limitation means exclusion of any expansion or changes of the standard method (e.g., addition of parameters or sample matrix types not listed).

Normative references

This clause lists a number of other standard methods essential for the application of the standard. Draft International Standards may also be cited in the list. All other documents, for instance any used for the development of the standard, may be listed in an informative bibliography (ISO, 1998a).

Interferences

This section gives information on the technical limitations of the standard method caused by, for example, sample matrix effects (coloured samples can interfere with the photometric detection or element specific spectral interferences (AAS, ICP-OES) or chemical interferences (precipitation reactions, formation of reaction by-products). These details are validated experimentally in laboratories participating actively in the standardization work. The documentation of the interferences may help potential users of a specific standard to decide whether the standard method could be applicable for the requirements of their analytical businesses.

Principle

This clause gives a brief overview of the procedural basis of the analytical method.

Reagents

This clause contains a list of reagents and/or solutions used in the method (ISO/IEC, 2001) including information on the required purity grade as well as concentrations of solutions.

Apparatus

This section defines the analytical system to be used for the determination of the parameters listed in the title of the standard (ISO/IEC, 2001). The suitability of the specified apparatus has also been checked experimentally. Standards developers

generally check different technical systems and appropriate alternative equipment, if this exists. Finally, the standards developers (working group members) decide which one of the possible alternative systems shall be part of the normative body of the standard. If applicable, alternative systems can be presented in an informative annex.

CEN and ISO standard developers should not refer to a sole supplier (monopoly situation). Equipment offered by a single manufacturer should not be specified. Where such equipment is not commercially available, detailed specifications for the equipment shall be given in order to enable all users to test comparable apparatus and systems (ISO/IEC, 2001).

Sampling and sample pre-treatment

Generally, this clause refers to an international standard, if such exists. If necessary, specific preconditions and methods of sampling or pre-treatment steps for the preservation of the samples (e.g., filtration, acidification, bottle material, storage conditions) are given.

Procedure

This clause gives advice about all of the procedural elements used for determination of the parameters. This includes the preparation of the test sample, the set-up procedure of the analytical system, the calibration strategy, and the measurement of the sample.

Calculation

This element gives instructions on how to convert a measured value obtained from the parameter of interest into a mass concentration, including the method of calculation (e.g., use of the inverse calibration function, consideration of blank values).

Expression of results

This clause defines the report format of the calculated results (e.g., dimension, number of significant figures).

Test report

The test report contains a minimum of information on the sample (e.g., result, identification data of the sample, applied standard method).

Interlaboratory trial

The presentation of statistical results of data from interlaboratory trials can be handled differently in CEN and ISO. CEN presents these data generally in the normative body of the standard, whereas ISO puts them in the informative annex of the standard. Besides the different philosophies in ISO and CEN on the layout of a standard, the organization and evaluation of an interlaboratory trial is obligatory for the standard developers in CEN and ISO, and the quality of the statistical data from the interlaboratory trial is the final categorical factor in the decision to publish the standard method, to postpone or to withdraw the project from the working list. The criteria for interlaboratory trial data to be met are given in ISO 5725, Part 2 (ISO, 2002).

1.3.7 EU Requirements for Standard Methods

General

Analytical methods used for the control procedures according to the European drinking water directive must be capable of measuring concentrations equal to the parametric value (Council Directive 98/83/EC, 1998). This is a positive requirement and enables laboratories to choose a suitable method among alternatives. The European directive additionally specifies quality requirements concerning trueness, precision, and the limit of detection of the method (see Table 1.3).

The performance characteristics of a method, obtained from an interlaboratory trial (see above), give a first indication of the suitability of an analytical method.

Table 1.3 Parameters with specified performance characteristics

	Trueness	Precision	Limit of detection
Parameters	% of parametric value		
Anions and Oxidizability			
Cl^-, CN^-, Cr(VI), F^-, NO_3^-, NO_2^-, SO_4^{2-}	10	10	10
BrO_3^-	25	25	25
TOC	25	25	10
Elements and Ammonium			
Al, As, B, Cd, Cu, Fe, Mn, Na, Ni, Pb, Se, NH_4^+	10	10	10
Hg	20	10	20
Sb	25	25	25
Organic parameters			
1,2-Dichloroethane, tetrachloroethene, trichloroethene, trihalomethanes (total)	25	25	10
Benzo(*a*)pyrene, benzene, pesticides, PAHs	25	25	25

However, it is the duty of the laboratory to validate each of the methods applied for drinking water analyses and to demonstrate the capability of the laboratory to fulfill the required characteristics according to the EU directive (Council Directive 98/83/EC, 1998).

Estimation of trueness and precision The EU directive (Council Directive 98/83/EC, 1998) refers to the definitions for the determination of trueness and precision given in ISO 5725-1 (ISO, 2002). According to this standard, the estimation of the trueness requires 'a large series' of replicate determinations of test samples. But what does 'large series' mean? Neither ISO 5725-1 nor the EU directive resolve this question. The determination of precision also requires a number of replicate determinations of a test sample. Information on a recommended number of replicates is also missing in ISO 5725-1.

A practicable concept is ENV-ISO 13530 (ENV/ISO/TR, 1998). ENV-ISO 13530 is a guide to analytical quality control (AQC). It is applicable to the chemical and physicochemical analysis of waters including drinking water. It describes an AQC concept applicable to analyses carried out frequently or infrequently as well as for complex, time-consuming, procedures producing only few results at a time (e.g., for the determination of complex organic contaminants).

For the estimation of trueness, ENV-ISO 13530 recommends regular participation in external quality procedures such as interlaboratory trials and proficiency schemes for the control of trueness (bias). For internal routine action, the use of control charts, based on the mean, spiking recovery, and analysis of blanks, is recommended. In addition, the standard recommends the use of a mean and/or a range control chart and the execution of a minimum of six replicate determinations of the test sample for the calculation of the standard deviation for the control of the precision.

Limit of detection The EU directive 98/93/EC (see Table 1.3) sets a requirement to be met for the limit of detection (LOD). The determination of the LOD does not follow a standard method. LOD shall be calculated from replicate determinations, either

(a) multiply the within-batch standard deviation of the reproducibility of a natural sample containing a low concentration of the parameter three times, or

(b) multiply the within-batch standard deviation of the reproducibility of a blank solution five times.

Information on a recommended number of replicates is missing in the directive (Council Directive 98/83/EC, 1998).

The LOD represents a qualitative performance data of the method, only. In contrast to the LOD, the Limit of Quantification (LOQ) would represent data valid for carrying out quantitative determinations. For this reason a revised directive (Council Directive 98/83/EC, 1998) should refer to the LOQ. It is intended to define a calculation procedure for LOQ with the publication of the revised ISO 13530 (ENV/ISO/TR, 2004).

As long as the lowest limit of application of the method is significantly lower than the required LOD, additional experiments for the estimation of the LOD do not need to be carried out. This attribute will be the case for the determination of many anions and cations (see later, Tables 1.5 and 1.6).

Examples for the estimation of laboratory internal performance data ENV-ISO 13530 (ISO/TR, 2003) can be applied to ascertain the laboratory internal values for precision, trueness and LOD according to the EU directive 98/83/EC. The examples in Table 1.4 may give an indication for the internal actions to be applied by the laboratory.

Table 1.4 Example for the estimation of performance characteristics for bromate

Demand for:	Recommended action:
Parametric value 10 μg/l	Execution of a practicable calibration according to ISO 8466-1 (1990) or ISO 8466-2 (2001), e.g. working range 2.5 μg/l to 25 μg/l BrO_3^-
Precision 2.5 μg/l	For frequent determinations: Use the standard deviation of a mean control chart (use of a 10 μg/l BrO_3^- control solution) For infrequent determinations: Calculate the standard deviation from the results of >6 replicate determinations of a 10 μg/l BrO_3^- standard solution *Note*: Whenever available, certified reference materials should be used.
Trueness 2.5 μg/l	*General*: participation in interlaboratory trials, regularly For frequent determinations: Operation of a mean control chart, concentration of the control solution e.g. 10 μg/l BrO_3^- Operation of a recovery control chart, when systematic errors from matrix interferences are expected Measurement of two blank solutions at the beginning and at the end of a batch in order to identify contamination of reagents, of the measurement system and instrumental faults and documentation of the blank values on a blank control chart For infrequent determinations: Measurement of trueness control samples in the lower and upper part of the calibrated working range Replicate measurements of samples Measurement of blanks Measurement of reference material, if available Validity check of the calibration function using material from an independent source
LOD 2.5 μg/l	Inclusion of the LOD value in the calibrated working range (e.g. 2.5 μg/l to 25 μg/l BrO_3^-)

It can be expected that the repertoire of actions recommended in Table 1.4 will be appropriate for the determination of inorganic parameters. For multistage or lengthy procedures that produce only few results at a time, the procedures for infrequent determinations could be carried out. However, this is still problematic for the determination of the performance characteristics for several (ecological important) pesticides where suitable reference materials of appropriate concentration are not available or the LOD requirement are unlikely to be achieved (Council Directive 98/83/EC, 1998).

CEN and ISO standard methods for drinking water analyses

CEN and ISO have already published a number of standard methods suitable for the determination of most of contaminants for the control of the quality of water. For the determination of anions and elements several alternative single and multiple component methods have been approved. For the determination of organic parameters generally multiple-component procedures are available.

Single-component methods are valid for that parameter cited in the scope of the standard, only. Generally, a single-component method requires parameter specific descriptions like sampling procedure, sample preservation and preparation, chemical reaction procedures, and measurement steps. Examples for typical single-component procedures are photometric, electrometric, or atomic absorption spectrometric (AAS) methods. The capital cost for the apparatus is relatively low. However, the obligatory procedural steps may be time consuming and labour intensive.

Multiple component methods are procedures for the determination of more than one parameter at a time. In contrast to single component methods multiple component methods describe a general procedure on sampling, preservation, preparation, and determination for all of the parameters in the scope of the method. Examples for typical multiple component procedures are inductively coupled plasma (ICP-OES or ICP-MS) for element analyses and chromatographic techniques (IC, GC, HPLC). The cost of the apparatus can be very high. However, multiple-component procedures for the determination of inorganic parameters are time saving and labour saving, and offer very high sample throughputs for the laboratories. They are considered to be very cost effective. Multistage procedures like trace level analyses of organic parameters can be time consuming, producing only a few results at a time.

Tables 1.5 to 1.7 present a selection of chemical and indicator parameters with specified requirements according to the EU drinking water directive (Council Directive 98/83/EC, 1998). In Tables 1.5 to 1.7 are listed the parameter, the parameter specific defined maximum contaminant levels, and limits of detection (LOD).

Also listed are recommendations for the application of existing CEN and ISO methods, generally automated multiple-component procedures, suitable for routine analyses with high sample throughput, except for standard methods for the determination of organic parameters which could be time consuming. Nevertheless, any laboratory can choose any alternative method of its choice as long as it is capable of

Table 1.5 Anions and Oxidisability (TOC)

Parameter	Method	Principle[a]	Working range[a] (mg/l)	Parametric value[a] (mg/l)	LOD[a] (mg/l)
Bromate	EN ISO 15061 (2001)	IC	≥0.0005	0.01	0.0025
Chloride	EN ISO 10304-1 (1995)	IC	≥0.1	250	25
Chromium(VI)	ISO/DIS 23913 (2004a)	CFA	≥0.002	0.05	0.005
Cyanide, total	EN/ISO 14403 (2002)	CFA	≥0.01	0.05	0.005
Fluoride	EN ISO 10304-1 (1995)	IC	≥0.1	1.5	0.15
Nitrate	EN ISO 10304-1 (1995)	IC	≥0.1	50	5
Nitrite	EN ISO 10304-1 (1995)	IC	≥0.05	0.5	0.05
Sulfate	EN ISO 10304-1 (1995)	IC	≥0.1	250	25
Total organic carbon (TOC)	EN 1484 (1997a)	Thermic catalytic oxidation	≥1	5	0.5

[a] where:
Parametric value is the required limit according to Council Directive 98/83/EC, 1998.
CFA is continuous flow analyses.
IC is ion chromatography.
LOD is the limit of detection, to be achieved according to Council Directive 98/83/EC, 1998.
Working range is the lowest determinable concentration stated in the method.

Table 1.6 Elements and ammonium

Parameter	Method	Principle[a]	Working range[a] (μg/l)	Parametric value[a] (μg/l)	LOD[a] (μg/l)
Aluminium	EN/ISO 17294-2 (2004)	ICP-MS	≥5	200	20
Ammonium	EN/ISO 14911 (1998)	IC	≥100	500	50
Antimony	EN/ISO 17294-2 (2004)	ICP-MS	≥0.2	5	1.25
Arsenic	EN/ISO 17294-2 (2004)	ICP-MS	≥1	10	1
Boron	EN/ISO 17294-2 (2004)	ICP-MS	≥10	1000	100
Cadmium	EN/ISO 17294-2 (2004)	ICP-MS	≥0.5	5	0.5
Copper	EN/ISO 17294-2 (2004)	ICP-MS	≥2	2000	200
Iron	EN/ISO 11885 (1997b)	ICP-OES	≥20	200	20
Lead	EN/ISO 17294-2 (2004)	ICP-MS	≥0.2	10	1
Mercury	EN 1483 (1997c)	AAS	≥0.1	1	0.1
Nickel	EN/ISO 17294-2 (2004)	ICP-MS	≥1	20	2
Selenium	ISO 9965 (1993)	AAS	≥1	10	1
Sodium	EN/ISO 17294-2 (2004)	ICP-MS	≥10	200 000	20 000

[a] Where:
AAS is atomic absorption spectrometry.
IC is ion chromatography.
ICP is inductively coupled plasma.
LOD is the limit of detection, to be achieved according to Council Directive 98/83/EC, 1998.
MS is mass spectrometry.
OES is optical emission spectrometry.
Parametric value is the required limit according to Council Directive 98/83/EC, 1998.
Working range is the lowest determinable concentration stated in the method.

Table 1.7 Organic parameters

Parameter	Method	Principle[a]	Working range[a]	Parametric value[a]	LOD[a]
Acrylamide	No standard method available in CEN/ISO	To be controlled by product specification		0.1	
Benzene	ISO 11423 (1997a,b)	GC-FID	≥1	1	0.25
Benzo(*a*)pyrene	EN/ISO 17993 (2003b)	HPLC-FD	≥0.005	0.01	0.0025
1,2-Dichloroethane	EN/ISO 10301 (1997d)	GC-ECD	≥5	3	0.3
Epichlorohydrin	EN 14207 (2003a)	GC-MS	≥0.1	0.1	
		To be controlled by product specification			
Pesticides[b]	ISO/EN 11369 (1997e)	HPLC-UV	≥0.1	0.1	0.025[c]
	EN/ISO 15913 (2003c)	GC-MS	≥0.05		
	EN/ISO 6468 (1996)	GC-ECD	≥0.01		
Polycyclic aromatic hydrocarbons	EN/ISO 17993 (2003b)	HPLC-FD	≥0.005	0.1	0.025
Tetrachloroethene	EN/ISO 10301 (1997d)	GC-ECD	≥0.1	10	0.1
Trichloroethene	EN/ISO 10301 (1997d)	GC-ECD	≥0.1	10	0.1
Trihalomethanes, total	EN/ISO 10301 (1997d)	GC-ECD		100	10
Vinyl chloride	No standard method available in CEN/ISO	To be controlled by product specification		0.5	

[a] Where:
ECD is electron capture detection.
FD is fluorescence detection.
FID is flame ionization detection.
GC is gas chromatography.
HPLC is high performance liquid chromatography.
LOD is the limit of detection, to be achieved according to Council Directive 98/83/EC, 1998.
MS is mass spectrometry.
Parametric value is the required limit according to Council Directive 98/83/EC, 1998.
UV is ultra violet detection.
Working range is the lowest determinable concentration stated in the method.
[b] Several organic insecticides, herbicides, fungicides, nematocides, acaricides, algicides, rodenticides, slimicides, their relevant metabolites, degradation and reaction products. Only those pesticides which are likely to be present in a given supply need be monitored (Council Directive 98/83/EC, 1998).
[c] The LOD applies to each individual pesticide and may not be achievable for all pesticides at present (Council Directive 98/83/EC, 1998).

meeting the method performance requirements of the EU directive (Council Directive 98/83/EC, 1998). The third column gives information about the analytical principle and the fourth column indicates the lowest concentration determinable cited in the standard method.

Methods for anion analysis For the determination of anions (except chromate and cyanide), ion chromatographic methods can be applied, because they were developed especially for drinking water analysis. The cited standards and drafts (see Table 1.3)

can be used for the control of the parametric value. For chromium determinations now the new ISO 18412 (ISO, 2005) is suitable for the control of the parametric chromium value of 50 μg/l (see Table 1.5), and the required LOD of 5 μg/l could be achieved by the method. The alternative sensitive CFA draft standard method ISO/DIS 23913 (ISO/DIS, 2004) is expected to be published soon. Both methods are applicable for the determination of chromate concentrations ≥2 μg/l and meet the requirements of the EU directive (Council Directive 98/83/EC, 1998). Reference to the CFA method is given due to the economic advantages of the CFA method (high sample through put).

Methods for elemental analyses For the determination of elements (e.g., lead, cadmium, etc.) the method of ICP-MS (EN Standard, 2004) should be preferred over AAS methods, whenever possible. The ICP-MS determination of iron could be subject to polyatomic interferences so the ICP-OES EN Standard, 1997b method should be applied. For mercury and selenium AAS hydride techniques (EN Standard, 1997c; ISO, 2003b) should be applied due to the higher sensitivity of these techniques compared with the ICP-MS technique (EN Standard, 2004). All of the cited standards (see Table 1.5) can be used for the control of the parametric value.

Methods for organic compounds analyses The very low parametric values for the organic compounds specified in the European directive 98/83/EC require methods suitable for trace level analyses. There is still demand for the development of new standard methods, because no CEN or ISO standard is currently available for the determination of acrylamide, several pesticides, and vinyl chloride.

HPLC-MS and GC-MS techniques have advantages for the determination of organic contaminants due to their high selectivity and sensitivity. For the determination of pesticides, the user has to apply several standards applicable for selected pesticides.

For the determination of highly volatile halogenated hydrocarbons, the GC-MS technique has not been included explicitly in the principles of EN ISO 10301 (EN/ISO, 1997d), so reference is made to the ECD-technique.

The laboratory shall ensure that it can meet the specified parametric values. This could, however, be a problem for the determination of, for instance, 1,2-dichloroethane and benzo(*a*)pyrene.

Alternative test methods Due to the relative high parametric values for chloride, iron, nitrate, nitrite, and sulfate, for example (see Tables 1.5 and 1.6), laboratories should consider the application of alternative methods for the measurements. Compared with reference and laboratory standard methods, the so-called ‘ready-to-use methods’, such as cuvette tests, allow fast and often inexpensive results, as well as needing reduced quantities of reagents and less waste. Provided they give reliable results, these alternative methods could be considered for use in drinking water analysis. ISO 17381 (ISO, 2003c) lists criteria and requirements for the producers and for the users of these tests.

REFERENCES

Council Directive 98/83/EC, 1998. Quality of water intended for human consumption, 3 November 1998, *Official Journal of the European Communities*, Volume 41, 5.12.2998, L 330, 32-54.

DIN, 1998. *A Word about DIN*, Berlin, 1998.

EN Standard, 1995. EN/ISO 10304-1:1995: Water quality – Determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulfate ions, using liquid chromatography of ions, Part 1: Method for water with low contamination (ISO 10304-1:1992) (under revision: ISO/CD 10304:2004-24-11).

EN Standard, 1996. EN/ISO 6468:1996 Water quality – Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes: Gas chromatographic method after liquid–liquid extraction (ISO 6468:1996).

EN Standard, 1997a. EN 1484:1997 Water analysis – Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC).

EN Standard, 1997b. EN/ISO 11885:1997 Water quality – Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy (ISO 11885:1996) (under revision).

EN Standard, 1997c. EN 1483:1997 Water quality – Determination of mercury.

EN Standard, 2001. EN/ISO 15061:2001 Water quality – Determination of dissolved bromate – Method by liquid chromatography of ions (ISO 15061:2001).

EN Standard, 2003a. EN 14207:2003 Water quality – Determination of epichlorohydrin.

EN Standard, 2003b. EN/ISO 17993:2003 Water quality – Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid–liquid extraction (ISO 17993:2002).

EN Standard, 2003c. EN/ISO 15913:2003 Water quality – Determination of selected phenoxyalkanoic herbicides, including bentazones and hydroxybenzonitriles by gas chromatography and mass spectrometry after solid phase extraction and derivatization (ISO 15913:2000).

Environmental Protection Agency, 2004a. *List of Contaminants and their MCLs*, US Environmental Protection Agency, Washington, DC. http://www.epa.gov/safewater/mcl.html#mcls

Environmental Protection Agency, 2004b. Title 40, Chapter 1, Part 143: *National Secondary Drinking Water Regulations.* US Environmental Protection Agency, Washington, DC. http://www.access.gpo.gov/nara/cfr/waisidx_02/40cfr143_02.html

Environmental Protection Agency, 2004c. *Six-Year Review of Drinking Water Standards.* US Environmental Protection Agency, Washington, DC. http://www.epa.gov/safewater/review.html

Environmental Protection Agency, 2004d. *Total Coliform Rule and Potential Revisions and Distribution System Requirements*. US Environmental Protection Agency, Washington, DC. http://www.epa.gov/safewater/tcr/tcr.html

Environmental Protection Agency, 2004e. *Drinking Water Priority Rulemaking: Microbial and Disinfection Byproduct Rules.* US Environmental Protection Agency, Washington, DC. http://www.epa.gov/safewater/mdbp/mdbp.html

Environmental Protection Agency, 2004f. *Drinking Water Contaminant Candidate List*. US Environmental Protection Agency, Washington, DC. http://www.epa.gov/safewater/ccl/cclfs.html

Environmental Protection Agency, 2004g. *National Contaminant Occurrence Data Base*. US Environmental Protection Agency, Washington, DC. http://www.epa.gov/safewater/data/ncod.html

Environmental Protection Agency, 2004h. *Unregulated Contaminant Monitoring Rule*. US Environmental Protection Agency, Washington, DC. http://www.epa.gov/safewater/ucmr.html

Environmental Protection Agency, 2004i. *Analytical Methods for Drinking Water*. US Environmental Protection Agency, Washington, DC. http://www.epa.gov/safewater/methods/methods.html

Environmental Protection Agency, 2005. *Drinking Water Contaminant Candidate List 2; Final Notice.* US Environmental Protection Agency, Washington, DC. 24 *FR* 9071 www.epa.gov/fedrgster/EPA-WATER/2005/February/Day-24/w3527.html.

International Standards Organization, 1990. Water quality – Calibration and evaluation of analytical methods and estimation of performance characteristics, Part 1: Statistical evaluation of the linear calibration function. ISO 8466-1:1990.

International Standards Organization, 1993. Water quality – Determination of selenium: Atomic absorption spectrometric method (hydride technique). ISO 9965:1993.

International Standards Organization, 1997a. Water quality – Determination of benzene and some derivatives, Part 1: Head-space gas chromatographic method. ISO 11423-1:1997.

International Standards Organization, 1997b. Water quality – Determination of benzene and some derivatives, Part 2: Method using extraction and gas chromatography. ISO 11423-2:1997.

EN Standard, 1997d. Water quality – Determination of highly volatile halogenated hydrocarbons: Gas-chromatographic methods. (EN/ISO 10301:1997).

EN Standard, 1997e. Water quality – Determination of selected plant treatment agents: Method using high performance liquid chromatography with UV detection after solid–liquid extraction. (EN/ISO 11369:1997).

International Standards Organization, 1998a. Model manuscript of a Draft International Standard, Version 1.2.

EN Standard, 1999. Water quality – Determination of dissolved Li^+, Na^+, $NH4^+$, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+} using ion chromatography: Method for water and waste water. (EN/ISO 14911:1999).

International Standards Organization, 2001. Water quality – Calibration and evaluation of analytical methods and estimation of performance characteristics, Part 2: Calibration strategy for non-linear second-order calibration functions. ISO 8466-2:2001.

International Standards Organization, 2002. Accuracy (trueness and precision) of measurement methods and results, Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method. ISO 5725-2:1994, corrigendum 1.

EN Standard, 2002. Water quality – Determination of total cyanide and free cyanide by continuous flow analysis. (EN/ISO 14403:2002).

EN Standard, 2004. Application of inductively coupled plasma mass spectrometry (ICP-MS), Part 2: Water quality – Determination of 62 elements. (EN/ISO 17294-2:2004).

International Standards Organization, 2003c. Water quality – Selection and application of ready-to-use test kit methods in water analysis. ISO 17381:2003.

International Standards Organization, 2004. *Guidelines for the Implementation of the Agreement on Technical Co-operation between ISO and CEN* (Vienna Agreement), Fifth edition.

International Standards Organization, CEN, 2001. *Agreement on Technical Co-operation Between ISO and CEN* (Vienna Agreement), Version 3.3.

International Standards Organization/DIS, 2004. Water quality – Determination of chromium(VI) and the sum of chromium(III) and chromium(VI): Method using flow analysis (FIA and CFA) and spectrometric detection. ISO/DIS 23913:2004.

International Standards Organization, 2005. Water quality – Determination of chromium(VI): Photometric method for low contaminated water. ISO/DIS 18412:2005.

International Standards Organization/IEC, 1995. *Directives, Part 1: Procedures for the technical work*, Third edition.

EN Standard, 2005. *General Requirements for the Competence of Testing and Calibration Laboratories* (under revision). (EN/ISO 17025:2005).

International Standards Organization/IEC, 2001. *Directives, Part 2: Rules for the Structure and Drafting of International Standards*, Fourth edition.

International Standards Organization/TC, 2003. Water Quality, *Report of the Secretariat ISO/TC 147*, Document ISO/TC 147 N 575.

EN Standard, 1998. Water quality – Guide to analytical quality control for water analysis water analysis. (EN/ISO/TR 13530:1998) (under revision: ISO/WD 13530).

National Drinking Water Advisory Council, 2004. *Report on the CCL Classification Process to the US Environmental Protection Agency*. National Drinking Water Advisory Council, Washington, DC. http://www.epa.gov/safewater/ndwac/pdfs/report_ccl_ndwac_07-06-04.pdf

National Research Council, 2001. *Classifying Drinking Water Contaminants for Regulatory Consideration*. National Research Council Committee on Drinking Water Contaminants, National Academy Press, Washington, DC.

2
Bromate Determination

A.-Hakim R. Elwaer, Philippe Quevauviller, K. Clive Thompson and **Cameron W. McLeod**

Analytical Methods for Drinking Water: Advances in Sampling and Analysis Edited by P. Quevauviller and K. C. Thompson © 2006 John Wiley & Sons, Ltd. ISBN: 0-470-09491-5

2.1 INTRODUCTION

The ozonation of water containing bromide generates the formation of several by-products, among which bromate is of particular concern. This substance is regulated by the European Directive on the quality of water intended for human consumption, which has fixed a maximum admissible concentration of 10 μg/L of bromate in drinking water (Council Directive 98/83/EC, 1998). Bromate determination has to be carried out using techniques with detection limits at or below 2.5 μg/L of bromate. This requirement for method sensitivity has highlighted the need for the development of methods that allow the control of the implementation of the regulation (Ingrand *et al.*, 2002).

A wide range of methods exists for determining bromate at the sub-μg/L level to mg/L levels. Most of them have been developed or adapted to meet the objectives of regulations setting up a bromate quality standard, for example in the 1990s the US EPA established a maximum permissible value in the range of 0.1–1 mg/L and analytical methods were first developed to meet this objective. The newly proposed quality standard of 10 μg/L has represented an analytical challenge, which has led to focusing on improvement of the sensitivity within the last few years (Guinamant *et al.*, 2003).

Official methods for bromate determination have been established by regulatory organizations, and one of these methods is ion chromatography with conductivity detection (IC/CD). As an example, the US Environmental Protection Agency (EPA) issued method 300.0 in 1989, which enables a bromate detection limit of 20 μg/L to be achieved (EPA, 1991). This method was, however, faced with interference problems for the analysis of drinking waters containing high levels of chloride (>50 mg/L). This necessitated efforts to improve the sensitivity of the technique, which was achieved either through an improvement in columns technology, enabling a reduction in the detection limit to 1.3 μg/L (EPA, 1997), or to development of sample pre-treatment for removing the main interference (chloride, sulphate and metals), leading to the detection limit being reduced to 0.5 μg/L using the ISO 15061 standard method (ISO, 2000).

Recent work has shown that the sensitivity of bromate analytical methods may be further improved by coupling the separation of bromate by ion chromatography with a specific post-column reaction (Ingrand *et al.*, 2002; Weinberg *et al.*, 2003). Also, inductively coupled plasma mass spectrometry (ICP-MS) linked to ion chromatography or flow injection systems with on-line separation of bromate on alumina microcolumns, enabled detection limits in the range 0.1–0.3 μg/L of bromate to be reached (Elwaer A.R. *et al.*, 1996). Detection limits have been further lowered to 0.05 μg/L by using an ultrasonic nebulizer (Creed *et al.*, 1996) and negative thermal ionization isotope dilution mass spectrometry (NTI-IDMS) (Diemer and Heumann, 1997). Finally, electrospray ion chromatography–tandem mass spectrometry (IC/MS-MS) enabled a detection limit of 0.03 μg/L to be achieved (Diemer and Heumann, 1997; Charles *et al.*, 1996).

From these observations, it could be concluded that these techniques meet legislation requirements. However, they all present complex and sometimes

time-consuming procedures, making them prone to error in case of insufficient handling care, and not sufficiently robust for on-site routine monitoring. Cost-effectiveness is another important consideration.

The need for ozone and bromate concentration monitoring in treated water on-site, however, implies that simple, low-cost and robust methods should be available. In this respect, visible spectrophotometry has been shown to be well adapted to on-site determination in comparison with other non-chromatographic methods (Ingrand *et al.*, 2002). However, this technique is not capable of determining bromate at the μg/L level and is therefore not in accordance with European legislation (Ingrand *et al.*, 2002). Progress has been possible through the use of different phenothiazines, which led to detection limits of 0.7 to 2 μg/L (Farrell *et al.*, 1995) or the use of flow injection methods with chlorpromazine, which enabled a detection limit in the same range (0.8 μg/L) to be reached (Gordon *et al.*, 1994). Finally, fluorimetry was identified as being an interesting alternative to spectrophotometry.

Recent progress has been made in connection to the requirements of the Drinking Water Directive, aiming to define IC/CD interference and ways of removing them, and to automate the pre-treatment and injection steps in the framework of a research project funded by the European Commission (Guinamant *et al.*, 2000). This project also included the development of alternative laboratory methods and field methods. This chapter summarizes the main findings of this project on the basis of recent reports (Guinamant *et al.*, 2000; Ingrand *et al.*, 2002).

2.2 ION CHROMATOGRAPHIC METHODS

2.2.1 Identification and Removal of the Main Interferences

Inorganic and organic interferences were investigated with respect to the determination of bromate in natural and drinking waters by an ion chromatographic method (Guinamant *et al.*, 2000; Ingrand *et al.*, 2002). The tested interferences were of two types:

(i) High concentrations of substances that may have an influence on the pre-concentration step and thus have an adverse effect on bromate recovery.

(ii) Presence of compounds that may co-elute with the bromate peak and be detected by the conductivity detector, resulting in a positive interference.

Interference by major inorganic substances present in natural waters in various aqueous matrices were tested using different types of waters (ultrapure water, mineral waters, and filtered river water) which were spiked with 5 and 10 μg/L of bromate. These matrices were additionally spiked with known concentrations of inorganic anions. Pre-treatment cartridges were tested for the elimination of these compounds (Ingrand *et al.*, 2002). Subsequently, various potential organic and (minor) inorganic interferents were spiked to determine possible co-elution with the bromate peak. The studied substances included a range of anionic oxidation by-products such as organic

acids, reflecting the fact that bromate is formed during the ozonation of natural waters that also leads to the formation of such by-products. Other products known to be commonly present in ozonated and natural waters were also tested, such as sugars, amino acids, humic and fulvic acids.

Interference during the pre-concentration step

An initial evaluation of the method performance (repeatability, reproducibility) concluded that bromate recoveries (for spiking levels of 5 and 10 μg/L), a result outside the range 90–110 % could be considered as an interference for a given concentration of an interfering substance. In addition, a deviation of more than 5 % in the bromate retention time was also considered to indicate an interference (influencing the peak shape). Examples are decrease in bromate recoveries (in spiked ultrapure water) in the presence of 25 mg/L chloride concentration (decreasing to between 60 and 70 %), while minimal effects were observed for a chloride concentration of 20 mg/L. No significant effects were observed for nitrate levels between 0 and 100 mg/L (as NO_3^-) and sulphate levels up to 200 mg/L (Ingrand *et al.*, 2002). Bicarbonate was shown to influence both the bromate recovery and retention time. The retention time decreased (to 85 %) in the presence of 150 mg/L of HCO_3^-. It was noted that, at a 400 mg/L concentration of HCO_3^-, the recovery rate is still not affected but the retention time decreases to 31 %. At concentrations higher than 450 mg/L HCO_3^-, bromate analysis was considered impossible (Ingrand *et al.*, 2002). A mixture of the four anions mentioned above on 5 and 10 μg/L bromate concentrations indicated interferences at concentrations of 100 mg/L of nitrate, 200 mg/L of sulphate, 10 mg/L of chloride and 50 mg/L of bicarbonate. However, when considered separately these anions did not interfere at these levels.

These experiments demonstrated an important analytical feature, namely that bromate analysis cannot be performed directly for waters containing more than 50 mg/L of bicarbonate and 10 mg/L of chloride (which correspond to levels commonly found in natural waters), and that consequently a pre-treatment step is required. These results were confirmed by the analysis of natural river and mineral waters (Ingrand *et al.*, 2002).

Examples of removal of major inorganic interfering anions

Treatment for removing interfering anions is generally based on the use of cartridges (e.g. DIONEX cartridges). In this context Ingrand *et al.* (2002) tested a range of cartridges for removing interfering anions, such as, for instance, RP C18 cartridges (retaining organic matter), Ag cartridges (retaining halide ions, in particular chloride ions which interfere in bromate analysis), H cartridges (retaining metals and bicarbonate), and Ba cartridges (retaining sulphate). As a result of the tests, and depending on the quality of the water, the combinations of cartridges shown in Table 2.1 were recommended.

Table 2.1 Recommended cartridge combinations to remove major inorganic interfering anions

Combination 1 RP + Ba + Ag + H			Combination 2 RP + Ag + H			Combination 3 Ag + H		
Carbon	>	2 mg/L	Carbon	>	2 mg/L	Carbon	<	2 mg/L
Chloride	>	1 mg/L	Chloride	>	1 mg/L	Chloride	>	1 mg/L
Nitrate	>	100 mg/L	Nitrate	>	100 mg/L	Nitrate	<	100 mg/L
Bicarbonate[a]	>	25 mg/L	Bicarbonate[a]	>	25 mg/L	Bicarbonate[a]	>	25 mg/L
Sulphate[b]	>	100 mg/L	Sulphate	<	100 mg/L	Sulphate	<	100 mg/L

[a] Degassing should be employed for waters containing more than 100 mg HCO_3^-/L in order to eliminate interference in the retention time. Also, as the majority of waters have a higher concentration than this, for practical purposes degassing should be performed systematically.
[b] A single barium cartridge could be used for concentrations up to 1.5 g/L of sulphate, since it does not saturate.

Study of potential organic interference

Organic substances commonly present in natural waters may have strong interfering effects on bromate determinations. Systematic tests were carried out by (Ingrand *et al.* 2002) on effects of 10 mg/L of substances such as sugars, amino acids, urea, low-molecular-weight carboxylic acids likely to be formed through the ozonation process, albumin, humic and fulvic acid, phenol, bisulfite, cyanide, iron and manganese. This level is significantly above the usual concentrations found in waters and the study aimed to test the maximum interference against the background noise, interfering peaks close to the bromate retention time, and bromate recoveries and/or deviations from the baseline. Results of the experiments indicated that none of the compounds tested induced noticeable interfering effects.

2.2.2 Sample Pre-treatment Automation

As mentioned above, the only interfering effects identified on bromate determination were due to the presence of major inorganic anions, and this could be solved by using a proper combination of pre-treatment cartridges. Until recently, this type of pre-treatment had always been manually operated using commercially available disposable ion exchange columns (involving sample injection, elution and separation) followed by detection and quantification using a conductivity detector (see Figure 2.1) or an ultraviolet detector (Guinamant *et al.*, 2000). This manual operation is not without risk of error, and recent developments have enabled to be based this pre-treatment on an automated procedure (Wolfis and Brandt, 1997).

In the above approach, the sample is automatically directed through a single solid phase extraction (SPE) column (containing the same materials as the three manual disposable columns) using an automatic device, which then introduces the collected eluate to the ion chromatographic pre-concentration column where the components are subsequently eluted into the analytical column and separated (Figure 2.2).

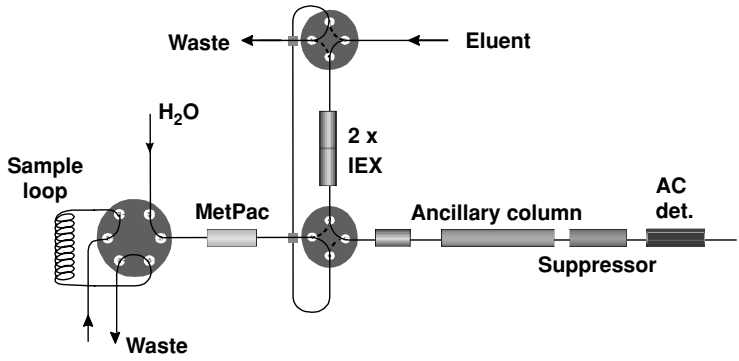


Figure 2.1 Ion chromatographic determination of bromate in water (after Ingrand *et al.*, 2002). Reprinted from Trends in Analytical Chemistry, Vol. 21, No. 1, Ingrand *et al.*, "Determination of bromate . . . ", pp. 1–12, 2002, with permission from Elsevier

Various experiments based on the measurement of calibration curve linearity, recovery assessment for various types of water, reproducibility and detection limits checks, etc., enabled the evaluation of the performance of the automated sample pre-treatment and injection system. The combined pre-treatment and injection of water samples into an ion chromatograph using the automatic SPE improved the overall reliability of the analysis while considerably enhancing the sample throughput (Guinamant *et al.*, 2000; Ingrand *et al.*, 2002). Recently a simple pre-concentration approach was developed using microwave energy for evaporation coupled with ion chromatography for bromate quantitation at 0.1 μg/L detection limits (Liu Y. and Mou S., 2002). Regulatory authorities have been continually validating standard methodologies for trace determination of bromate in waters. The US Environmental Protection Agency has developed a number of standard methods based on the use of

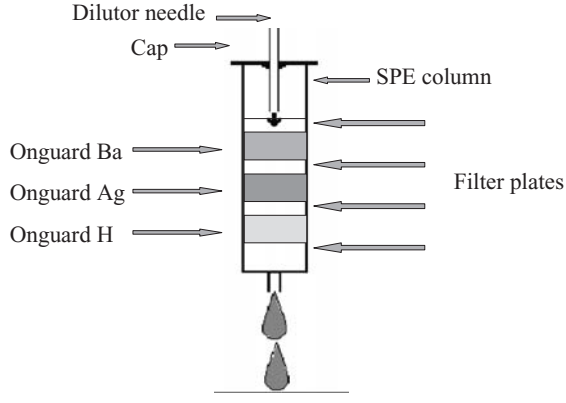


Figure 2.2 Solid phase extraction (SPE) column with three added exchange resins (after Ingrand *et al.*, 2002). Reprinted from Trends in Analytical Chemistry, Vol. 21, No. 1, Ingrand *et al.*, "Determination of bromate . . . ", pp. 1–12, 2002, with permission from Elsevier

ion chromatography. These methods were recently reviewed and various parameters evaluated (Hautman *et al.*, 2001).

2.3 ALTERNATIVE LABORATORY METHODS

2.3.1 Ion Chromatography / ICP-MS

Bromate determination may be carried out by coupling an ion chromatographic system to an inductively coupled plasma–mass spectrometry (ICP-MS) system. As shown by (Ingrand *et al.* 2002), this coupling requires an optimization procedure on a multi-element level, for which examples are found in the literature (Guinamant *et al.*, 2000). Experiments demonstrated that interference on the masses of the two bromine isotopes may occur from $^{38}Ar^{40}ArH$ for ^{79}Br and from $^{40}Ar^{40}ArH$ for ^{81}Br (Ingrand *et al.*, 2002). Considering that the natural abundance of ^{38}Ar is only 0.06 % of the natural abundance of ^{40}Ar, the background noise for ^{79}Br is much lower than for ^{81}Br and, consequently, sensitive detection of bromine species by ICP-MS is preferably done via the ^{79}Br isotope. The scheme of the whole experimental set-up for the determination of bromate by IC/ICP-MS is shown in Figure 2.3; additional details on IC and ICP-MS parameters and conditions are given by Ingrand *et al.* (2002). The method has been validated by comparison with a reference IC/CD method (French standard XP T 90-210), using the same criteria as in the automated system. The limit of detection is 0.1 μg/L of bromate without the pre-concentration

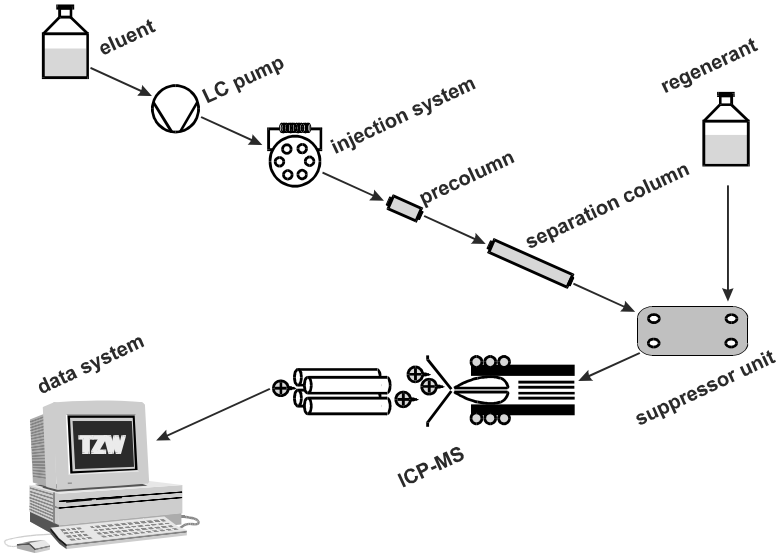


Figure 2.3 Experimental set-up for the IC/ICP-MS coupling (after Ingrand *et al.*, 2002). Reprinted from Trends in Analytical Chemistry, Vol. 21, No. 1, Ingrand *et al.*, "Determination of bromate . . . ", pp. 1–12, 2002, with permission from Elsevier

step. Repeatability and reproducibility of the method are at least comparable to the current IC/CD method. It constitutes a reliable technique and, due to the fact that no sample pre-treatment is necessary, the method is fast, the time for one complete analysis being less than 10 minutes.

2.3.2 Ion Chromatography Spectrophotometry Detection

This method is based on the hyphenation of an ion chromatographic system and a post-column reaction with spectrophotometry detection (IC/CLP). The post-column reaction involves chlorpromazine (CLP) and hydrochloric acid (Gordon *et al.*, 1994). After optimization of the operating conditions (concentration and reagent flow), the first investigations were carried out using a direct injection of samples with neither pre-treatment nor pre-concentration, followed by ion chromatography analysis. This led to a quantification limit of approximately 5 μg/L, which did not meet the requirement of the regulation (Ingrand *et al.*, 2002). An improvement in the detection limit could be achieved by a pre-concentration of the sample. As demonstrated by previous studies, the concentration step suffers from various interference, which requires pre-treatment of the samples prior to the pre-concentration stage. Analytical conditions and typical chromatograms obtained by conductivity (IC/CD) and visible photometric detection after post-column reaction (IC/CLP) are described by Ingrand *et al.* (2002).

The performance of the CLP post-column method was evaluated on three ozonated waters and five final waters (ozonated and then treated with sodium hypochlorite or chlorine dioxide) analysed simultaneously with the reference method (IC/CD) and the CLP post-column method (Table 2.2). The deviations obtained between alternative and reference methods were between 0 and 16 %. Highest deviations were observed with the conductivity detector in comparison with the alternative CLP

Table 2.2 Comparison between the reference method and the CLP post-column method in drinking waters, average of three replicates (after Ingrand *et al.*, 2002). Reprinted from Trends in Analytical Chemistry, Vol. 21, No. 1, Ingrand *et al.*, "Determination of bromate . . . ", pp. 1–12, 2002, with permission from Elsevier

	Concentration of bromate (μg/L)		Deviation
Type of water	IC/CD	IC/CLP	(%)
Ozonated water	5.7	5.1	11
Ozonated water	6.9	6.1	12
Ozonated water	7.0	6.7	4
Final water	2.5	2.1	16
Final water	3.7	3.8	3
Final water	12	11	8
Final water	15	14	7
Final water	18	18	0

post-column method (Ingrand *et al.*, 2002). The limit of detection and quantification were respectively 0.2 and 0.3 μg/L, of bromate. The calibration is linear from 0.5 to 20 μg/L, which fulfils the requirements of the latest European regulation.

In another work (Delcomyn, *et al.*, 2001; Weiberg, *et al.*, 2003) ion chromatography was coupled to post-column derivatization prior to UV spectrophotometric detection. In this study 25-mM H_2SO_4 and 0.145-mM $NaNO_2$ were employed to generate *in-situ* nitrous acid, which together with 2-M NaBr generated the tribromide ion in the presence of the eluting oxyhalides detectable at 267 nm. The practical quantitation limit for bromate using this approach is 0.05 μg/L. Earlier, Fuchsin reagent, acidified using HCl, was employed as an IC post-column derivatization reagent for bromate detection at 540 nm (Achilli and Romele, 1999). This method achieved a detection limit of 0.1 μg/L and a working range of 2–50 μg/L of bromate.

Three different post-column reaction methodologies based on ion chromatographic separation have been compared (Echigo *et al.,* 2001). The KI–$(NH_4)_6$ Mo_7O_{24} method, the NaBr–$NaNO_2$ method, and the *o*-dianisidine method showed similar detection limits (0.17, 0.19 and 0.24 μg/L) for bromate analysis with pneumatic reagent delivery systems. With respect to the simplicity of the system, the *o*-dianisidine method is the best option of the three. Also, it is of note that the NaBr–$NaNO_2$ method was considered to be susceptible to interference by matrix ions because of the use of a lower detection wavelength. It was also found that the *o*-dianisidine method can achieve a low μg/L level detection of nitrite with a simpler configuration (i.e., only one post-column reagent) than the KI–$(NH_4)_6Mo_7O_{24}$ method, while the sodium bromide–sodium nitrite method was not sensitive enough for nitrite analysis at the μg/L level. All three methods are compatible with conductivity detection. When used in combination with conductivity detection, this compatibility allows simultaneous analysis of bromate, nitrite, and other common ions in drinking water, such as bromide ions.

2.3.3 Ion Pair Chromatography – Fluorescence Detection

This method consists in the separation of bromate using ion-pair chromatography with post-column reaction and detection with a fluorescence detector (IP/Fluo). The registered signal corresponds to a decrease of fluorescence intensity. The post column reaction involves Carbostyril 124 in acidic conditions (Gahr *et al.*, 1998).

Two parameters were investigated with the aim of improving the reaction: (i) the temperature at which the post-column reaction is carried out (an important factor controlling the chemical reaction), and (ii) the reaction time. Increasing the temperature of the reaction coil from 20 °C to 60 °C significantly improved the efficiency of the post column reaction (Gahr *et al.*, 1998). With respect to the reaction time, the use of a longer reaction coil (15 m rather than 5 m) improved the sensitivity of the method by a factor of 3 (Figure 2.4).

The quantification limit of the method was 1.6 μg/L. This technique has been tested on several ozonated waters or samples after final disinfection with chlorine

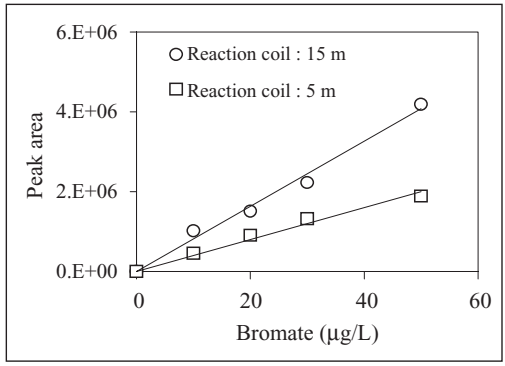


Figure 2.4 Importance of the post-column reaction time on the sensitivity of the fluorescence method (MilliQ water, Carbostyril 5×10^{-7} mol/L, 60 °C). (After Ingrand *et al.*, 2002). Reprinted from Trends in Analytical Chemistry, Vol. 21, No. 1, Ingrand *et al.*, "Determination of bromate . . . ", pp. 1–12, 2002, with permission from Elsevier

or chlorine dioxide, simultaneously with the current IC/CD method (Ingrand *et al.*, 2002). Results obtained from the fluorescence quenching system using Carbostyril 124 were in good agreement with the analyses conducted using IC/CD since the difference between the two techniques did not exceed 1 to 2 µg/L. However, this post-column reaction was affected by chlorite, the major chlorine dioxide by-product. Chlorate, the second largest chlorine dioxide by-product, was not found to interfere.

2.3.4 Flow Injection – ICP-MS

Flow injection (FI) provides a powerful approach to trace element analysis (Valcarcel and Luque de Castro, 1999; Sanz Medel, 1999). FI methodologies are realistic alternatives to ion chromatography and hence offer scope for extending and/or advancing analytical capabilities for bromate determination.

On-line reaction chemistry and traditional laboratory operations, including solid phase extraction, are readily implemented in the flow injection mode and analytical application extends from simple anion/cation determinations to drugs and biomolecules. Ultra-trace determination of bromate in waters has been achieved using a flow injection system having an alumina micro-column interfaced with an ICP-mass spectrometer (Elwaer *et al.*, 1996; Elwaer, 1999), which conferred a high degree of selectivity thanks to (i) the on-line separation/isolation of bromate from bromide and coexisting cations, and (ii) mass selective detection. High sensitivity could be obtained through on-line pre-concentration. Furthermore the alumina microcolumn ICP-MS system eliminated possible molecular ion interference caused by potassium content in the form of $^{40}Ar^{39}K$, thus enhancing the mass-to-charge signal at ^{79}Br. This is due to anionic affinity of the acidic alumina microcolumn, hence the K^+ cation is not retained, as demonstrated in Figure 2.5.

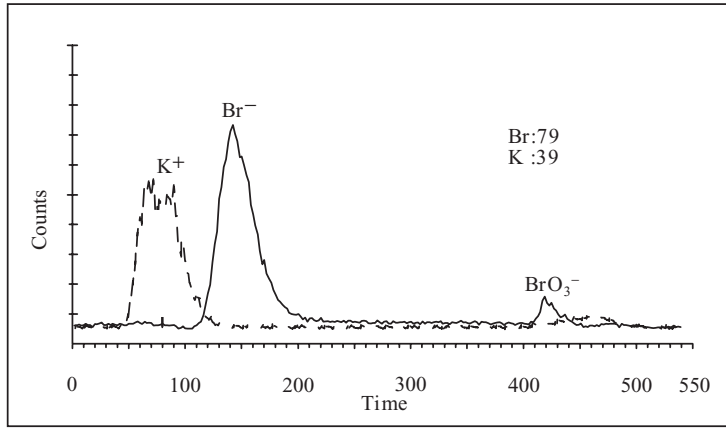


Figure 2.5 Ion time responses (overlays) at *m*/*z* 39 and *m*/*z* 79 for a spiked mineral water

A flow injection system with a micro-column of strong anion exchanger has been interfaced with an ICP-mass spectrometer via a microconcentric nebulizer to perform on-line separation and trace determination of bromate in drinking waters (Elwaer, 1999; Elwaer *et al.*, 2000). Method development studies examined the effect of sample injection volume, carrier stream flow rate and eluent concentration on system response. Basic performance data for this method were: limit of detection, 0.13 μg/L (500 μL sample injection); analysis time, 5 minutes per sample; precision, 2.6 % RSD (at 5 μg/L).

2.4 FIELD-BASED METHODS

2.4.1 Spectrophotometric Method with Methylene Blue

This method is based on the reaction between bromate and methylene blue in acidic conditions. The first step consists in the optimization of the operating condition (concentration of reagents, reaction time, wavelength, etc.) in order to obtain the best sensitivity (Ingrand *et al.*, 2002).

The robustness of the method has been tested with various matrices: spiked Evian water, ozonated waters and final waters (ozonated and then treated with sodium hypochlorite or chlorine dioxide). The results are compared in Table 2.3 in which matrices A to C naturally contained bromate whereas Evian water was spiked at 5 and 10 μg/L (Ingrand *et al.*, 2002). For Evian water and ozonated waters, concentrations obtained using the field method were in good agreement with the theoretical spiking. However, for final waters treated with sodium hypochlorite or chlorine dioxide, results showed that the disinfection step using sodium hypochlorite is a major source of interference (deviations from 460 to 744 %). Disinfection using chlorine dioxide leads to lower interference (deviation 19 %).

Table 2.3 Determination of bromate in Evian water and in three types of ozonated matrices: comparison between the reference technique (IC/CD) and the methylene blue method (after Ingrand *et al.*, 2002). Reprinted from Trends in Analytical Chemistry, Vol. 21, No. 1, Ingrand *et al.*, "Determination of bromate . . . ", pp. 1–12, 2002, with permission from Elsevier

Matrix	Treatment	Concentration in bromate (μg/L)		Divergence MB vs IC/CD (%)
		IC/CD or theoretical spiking	Methylene blue (MB)	
Evian	/	5	4	20
		10	9	10
A	O_3	31	30	3
	$O_3 + ClO^-$	27	151	460
B	O_3	10	12	20
	$O_3 + ClO^-$	18	152	744
C	O_3	23	23	0
	$O_3 + ClO_2$	16	19	19

O_3: Ozonation step.
ClO^-: Disinfection with sodium hypochlorite.
ClO_2: Disinfection with chlorine dioxide.
IC/CD: Ion chromatography with conductivity detection (reference method).

Several methods for removing hypochlorite ions are described in the literature (Gordon *et al.*, 1989; Fletcher and Hemmings, 1985), most of them being based on its oxidizing capacity. Among the tested compounds, only the hydroxylamine hydrochloride pre-treatment was effective in hypochlorite removal. In samples A and B, this pre-treatment suppressed hypochlorite interference. In low mineralized matrices, such as deionized water or sample C (treated with chlorine dioxide), hydroxylamine hydrochloride partially reduced bromate. The use of this agent seemed well adapted for bromate determination using methylene blue (Table 2.4). However, the pre-treatment conditions (concentration and reaction time) needed to be optimized according to the matrix to be analysed (Ingrand *et al.*, 2002).

Table 2.4 Determination of bromate in the presence of hypochlorite ions: evaluation of the hydroxylamine hydrochloride efficiency. Concentrations are in μg/L (after Ingrand *et al.*, 2002). Reprinted from Trends in Analytical Chemistry, Vol. 21, No. 1, Ingrand *et al.*, "Determination of bromate . . . ", pp. 1–12, 2002, with permission from Elsevier

Matrix	IC/CD	Field method (Methylene Blue 1 mg/L + HCl 2 mol/L)			
		Without pre-treatment	Deviation vs IC/CD (%)	With pre-treatment	Deviation vs IC/CD (%)
DW +25 μg/L BrO_3^-	25	24	−1	21	−16
A	27	151	460	32	19
B	18	152	744	22	22
C	16	19	19	15	−6

DW: Deionized water.
IC/CD: Ion chromatography with conductivity detection (reference method).

This method allows determination of bromate at concentration levels from 4 to 50 μg/L, with divergence between results obtained with both IC/CD (reference method) and methylene blue methods lower than 20 %. The high level of interference from hypochlorite ions has been demonstrated but it can be overcome by pre-treating samples with hydroxylamine hydrochloride. Such pre-treatment should be adapted to the matrix analysed on site (Ingrand *et al.*, 2002).

2.4.2 Flow Injection – Spectrophotometric Detection

With reference to bromate determination, there have been few published flow injection (FI) studies. Gordon *et al.* (1994) described a spectrophotometric procedure based on the oxidation of chlorpromazine (CLP). A low limit of quantitation (0.8 μg/L) was realized but the method was susceptible to interference by cations and other co-oxidants.

The flow injection system described by Gordon *et al.* (1994) was suitably adapted by incorporating an alumina micro-column into the manifold, resulting in an on-line pre-concentration/separation and spectrophotometry detection (Elwaer, 1999; Ingrand *et al.*, 2002). The main operational features are described elsewhere (Guinamant *et al.*, 2000; Ingrand *et al.*, 2002). Method development/optimization examined the effect of key flow-injection parameters on system response. Limit of detection was 0.85 μg/L (2mL sample volume, pre-concentration factor: 7) and precision at 10 μg/L was 0.5 % RSD. Of the potential interference tested, (NO_2^- 0.1 mg/L; NO_3^- 50 mg/L; SO_4^{2-} 100 mg/L; Br^- 1 mg/L; ClO_3^- 2 mg/L; Cl^- 100 mg/L; Fe^{3+} 2 mg/L), only nitrite gave a positive response, suggesting that it underwent deposition/elution on the alumina micro-column and oxidized chlorpromazine. Sample pre-treatment with sulphamic acid may be used to remove nitrite interference (Gordon *et al.*, 1994). Further development work and intercomparison with IC and FI/ICP-MS are needed prior to field testing.

2.5 STABILITY OF BROMATE

Previous sections of this chapter discussed the details of newly developed analytical methodologies and strategies for bromate separation and trace quantification. This confirms the current vast interest of the analytical community in bromate determination as a result of ongoing regulatory requirements. The acceptance of such methods depends mainly on the analytical performance as related to accuracy and precision. However, despite all analytical efforts, very little work has been done to investigate the stability of bromate species between sampling and analysis in different water matrices. Studies of bromate stability in water matrices should be carried out before any analytical methodology can be approved.

In this respect the European Commission set up a project on Development of Laboratory and Field Methods for Determination of Bromate in Drinking Water

(Guinamant *et al.*, 2000; Ingrand *et al.*, 2002). This project devised different work packages including stability of bromate in waters, followed by an inter-laboratory comparison exercise to evaluate and validate the developed methods.

Bromate stability was studied in two different dimensions. The first was related to direct evaluation of bromate stability in different water matrices. The second was devoted to stability of bromate species mobilized on activated alumina micro-columns with a view to developing a field sampling methodology from bromate in waters.

2.5.1 Effect of Water Matrix on Bromate Stability

Stability of chemical species during sampling, sample handling, transportation and storage prior to analysis has always been an issue of concern to analytical chemists. Chemical changes of analyte species can be influenced by various parameters including sampling methods, container material, chemical interference, conditions of handling, transportation and storage. Bromate is not considered to be among the naturally occurring brominated compounds and it must therefore be formed as a result of a chemical process. Once formed bromate will maintain its chemical structure unless exposed to a chemical reducing agent. However, water sampling for metals is normally accompanied by nitric acid stabilization which has been confirmed not to affect bromate chemical stability, as will be discussed in the following section (Elwaer *et al.*, 1996).

In this study, the stability of bromate in water samples with different matrix constituents was investigated. Water samples ranged from soft to hard and were spiked with 1 mg/L bromide, 0.5 mg/L chlorite and 0.5 mg/L chlorate. These levels are considered to be higher than those normally observed in waters for these three anionic species. Each sample was also spiked with 2.5, 10 and 25 μg/L of bromate. Furthermore, a 5 μg/L of bromate standard in deionized water was also prepared. Brown glass bottles capped with polypropylene tops and PTFE inserts were used as sample containers. Samples were stored in the dark at 4 °C. Tables 2.5 and 2.6 summarize matrix constituents of each sample, preservation method spike levels and results of analyses. The results clearly demonstrate that for the two high and low total hardness waters tested, samples containing 2.5 to 25 μg/L bromate were stable for at least 20 days and that the addition of 50 mg/L ethylenediamine (EDA) preservative did not affect the results, as illustrated in Table 2.6. The results also confirm that 5 μg/L bromate standard made up in deionized water had the same stability over this period.

The high total hardness stability tests were extended to more than 100 days and bromate results using the FI-ICP-MS method confirmed the stability of bromate over this period. Similarly the presence of 50 mg/L EDA preservative showed no effect on bromate stability. High total hardness water samples were further re-analysed after a period of 100 days and bromate content was found to be stable.

This study concluded that bromate concentrations are stable in hard waters for up to 100 days when stored in brown glass bottles in dark at 4 °C. It was also

Table 2.5 Soft and hard water samples investigated for bromate stability

No.	Sample constituents	Preservation technique	Total hardness (mg/L $CaCO_3$)	Spiked bromate concentration (μg/L)	Analysis schedule (days)
1	Spiked deionized water containing 1 mg/L bromide, 0.5 mg/L chlorite and 0.5 mg/L chlorate (added as KBr, $NaClO_2$ and $KClO_3$)	None	0	5	0, 2, 10, 20
2	Spiked hard water containing 1 mg/L bromide, 0.5 mg/L chlorite and 0.5 mg/L chlorate (added as KBr, $NaClO_2$and $NaClO_3$)	Addition of 50 mg/L of ethylenediamine (EDA)	273 hard water	0, 2.5, 10 and 25	0, 2, 10, 20
3	Spiked hard water containing 1 mg/L bromide, 0.5 mg/L chlorite and 0.5 mg/L chlorate (added as KBr, $NaClO_2$ and $KClO_3$)	None	273 hard water	0, 2.5, 10 and 25	0, 2, 10, 20
4	Spiked soft water containing 1 mg/L bromide, 0.5 mg/L chlorite and 0.5 mg/L chlorate (added as KBr, $NaClO_2$ and $NaClO_3$)	Addition of 50 mg/L of ethylenediamine (EDA)	115 soft water	0, 2.5, 10 and 25	0, 2, 10, 20
5	Spiked soft water containing 1 mg/L bromide, 0.5 mg/L chlorite and 0.5 mg/L chlorate (added as KBr, $NaClO_2$ and $KClO_3$)	None	115 soft water	0, 2.5, 10 and 25	0, 2, 10, 20

demonstrated that no preservative was needed to stabilize bromate in the stored water samples.

2.5.2 Stability of Bromate Species Immobilized on Alumina Microcolumns

The previous section addressed the effect of water matrix on bromate stability. This section investigates the possibility of developing an alternative approach to sampling of bromate species in waters by employing columns of a selective packing material. This study was based on the development of an FI system with alumina microcolumns

Table 2.6 Average results of bromate analysis in different waters spiked at 0, 2.5, 10 and 25 μg/L BrO_3^- and analysed at intervals of 0, 2, 10 and 20 days

			Average bromate over a 20-day period (0, 2, 10 and 20 days)	
Sample	Preservation technique	Spike level BrO_3^-(μg/L)	BrO_3^- (μg/L)	RSD (%)
Spiked deionized water containing 1mg/L bromide, 0.5 mg/L chlorite and 0.5 mg/L chlorate (added as KBr, $NaClO_2$ and $KClO_3$)	None	5.00	4.7	16.1
Spiked hard water containing 1 mg/L bromide, 0.5 mg/L chlorite and 0.5 mg/L chlorate (added as KBr, $NaClO_2$ and $NaClO_3$)	Addition of 50 mg/L of ethylenediamine (EDA)	0.0	1.4	61.1
		2.5	2.8	22.9
		10.0	9.8	10.0
		25.0	22.2	6.2
Spiked hard water containing 1 mg/L bromide, 0.5 mg/L chlorite and 0.5 mg/L chlorate (added as KBr, $NaClO_2$ and $KClO_3$)	None	0.0	1.0	—
		2.5	3.0	21.4
		10.0	9.2	10.1
		25.0	21.1	4.6
Spiked soft water containing 1 mg/L bromide, 0.5 mg/L chlorite and 0.5 mg/L chlorate (added as KBr, $NaClO_2$ and $NaClO_3$)	Addition of 50 mg/L of ethylenediamine (EDA)	0.0	—	—
		2.5	3.3	8.6
		10.0	10.8	6.1
		25.0	26.8	16.3
Spiked soft water containing 1 mg/L bromide, 0.5 mg/L chlorite and 0.5 mg/L chlorate (added as KBr, $NaClO_2$ and $KClO_3$)	None	0.0	—	—
		2.5	2.9	13.8
		10.0	10.2	7.3
		25.0	25.6	8.4

interfaced with ICP-MS and used to determine ultra-trace levels of bromate in drinking waters (Elwaer *et al*., 1996). In this approach, the ion-exchange properties of activated alumina were used to affect the on-line pre-concentration of bromate and rejection of any coexisting bromide (potential interference). As evidenced in the recent literature, including the aforementioned FI–ICP-MS study, micro-column technology is becoming an increasingly important trend in ultra-trace investigations

Table 2.7 Determination of bromate in charged microcolumns. Uncertainties, $\pm s$

	Bromate concentration	
Storage time	BrO_3^- μg/L	RSD (%)
1 hour	5.83 ± 0.22	3.81
1 day	5.76 ± 0.19	3.41
3 days	6.09 ± 0.16	2.56
1 week	6.16 ± 0.16	2.55
2 weeks	6.00 ± 0.22	3.63
3 weeks	6.34 ± 0.06	0.90
4 weeks	5.99 ± 0.31	5.25
8 weeks	6.86 ± 0.13	1.96

(Quevauviller, 1997). Moreover, in Hg and Cr speciation studies (Mena *et al.*, 1995, 1996) analyte-enriched microcolumns have been shown to offer a convenient route to instrument calibration and development as a new reference material (RM) format. With the latter in mind and given the urgent need to validate new methods for the determination of bromate in process and drinking waters, a batch of microcolumns was prepared and analysed over an 8-week period in order to assess bromate stability. Microcolumns of activated alumina ($n = 30$) were charged with bromate standard solution (0.5 ml, 6.0 μg/L) and stored at 4 °C in a light-tight container. Microcolumns were removed at regular time intervals (1 hour, 1 and 3 days and 1, 2, 3, 4 and 8 weeks) and bromate species were eluted and quantified by flow-injection ICP-MS. Analyte recoveries were found to be quantitative (96–101 %) and reproducible over the 8-week period. These results indicate that for trace level determinations (μg/L) of bromate, a micro-column format may provide a convenient and reliable route for delivery of external calibrants and reference materials. Analytical data for the complete study are summarized in Table 2.7. It is clear from these results that the column-to-column variability is low and that analyte recoveries are essentially quantitative, with good precision (short-term, RSD 0.9–5.3 %; long-term, RSD 3.3 %) for the 8-week period. It is concluded, therefore, that micro-columns of activated alumina provide a useful support for stabilizing bromate and as such provide a simple and convenient means for the delivery of precise quantities of bromate at the trace and ultra-trace level.

2.6 INTERLABORATORY EXCERCISE FOR BROMATE DETERMINATION

Toxicological studies of bromate have provided continuous evidence of its possible carcinogenicity (Kurokawa *et al.*, 1990). As a result a maximum admissible concentration (MAC) of 10 μg/L bromate in drinking waters is recommended by the US EPA (US EPA,1997), the European Commission (Council Directive 98/83) and the WHO (WHO, 1991), this limit has been defined primarily on the basis of the detection

Table 2.8 Bromate concentration in the five samples

Sample Number	Matrix	Bromate concentration (μg/L)			
		Natural background	Spike level	Total (target) level	Grand mean of all labs
1	Deionized water	0	5.7	5.7	5.38
2	High total hardness borehole water sample	< 0.3	2.7	2.7	2.62
3	Low hardness tapwater	1.1	7.5	8.6	8.70
4	Ozonylated final treated water	Not known	0	?	8.50
5	GAC treated water	~0.3[a]	4.0	4.0[a]	4.14

[a] Values given are mean concentrations in μg/L unless stated otherwise.

capabilities of existing ion chromatographic methodologies rather than on toxicological considerations. The EC recommends detection limits of less than 2.5 μg/L. This has called for the development of more sensitive and/or alternative techniques. A project funded by the Standards, Measurements and Testing Programme of the European Commission, and run jointly with the ISO group, on bromate analysis has enabled the improvement and/or development of methods for the determination of bromate at such concentration levels. Sections 2.2, 2.3 and 2.4 above discussed methods of bromate analysis and their analytical performance. This collaborative work was concluded by the organization of an interlaboratory trial involving 26 European laboratories, which enabled the testing of both a draft ISO standard method and alternative methods.

Five samples were prepared as test materials for the interlaboratory trial, of which the bromate content and matrix composition are given in Tables 2.8 and 2.9 respectively.

Samples 1, 2, 3 and 5 were spiked using a potassium bromate solution. It can be seen that the trial covered the concentration range 2–10 μg/L bromate. The proposed EC limit for bromate is 10 μg/L, thus the lower level of interest for regulatory bromate analysis is about 2.5 μg/L. A result very close to the detection limit of 0.3 μg/L was observed for sample 5, which was a granulated activated-carbon (GAC) treated water. This water had not been treated with ozone and it was felt that it was unlikely to contain bromate; thus a target value of 4.0 rather than 4.3 μg/L was used. The stability of bromate had been tested prior to the interlaboratory study as demonstrated in the previous section. Thirty-three sets of data were generated by 26 laboratories (some laboratories provided results for more than one method). Calibration was either by calibration graph or standard additions. Each participating laboratory received one bottle of each of the above five samples and a calibration solution containing 10 μg/L bromate. This latter solution was prepared from the 1000 mg/L bromate master calibration solution. The laboratories were requested to make a minimum of five replicate determinations on each sample on at least two different days. The

Table 2.9 Sample matrix analysis[a]

	Sample Number				
Determinand	1	2	3	4	5
Conductivity (μS/cm)	<10	567	197	347	202
Calcium (Ca)	<2	81.7	24.4	49.7	37.3
Magnesium (Mg)	<2	19.2	2.05	7.5	1.25
Total hardness ($CaCO_3$)	<5	283	70	155	97.5
Alkalinity (HCO_3)	<10	267	26	79	110
Chloride (Cl)	<10	41	14	21	6.1
Nitrate (NO_3)	<1	7.2	2.9	15.6	<1
Sulphate (SO_4)	<10	44	44	72	4.3
Total organic carbon (C)	<0.3	0.3	2.14	2.2	0.95
Bromide (Br)	<0.010	0.042	0.019	0.036	0.015
Chlorite (ClO_2^-)	<0.010	<0.010	<0.010	<0.010	<0.010
Chlorate (ClO_3^-)	<0.010	<0.010	0.07	<0.010	<0.010
Iron	<0.020	<0.020	0.043	<0.020	<0.020
Aluminium	<0.010	<0.010	0.025	0.059	<0.010
Manganese	<0.005	<0.005	<0.005	0.012	<0.005
Phosphorus (P)	<0.1	<0.1	0.82	<0.1	<0.1

[a] Values given are mean concentrations in mg/L unless stated otherwise.

laboratories were instructed to use their own calibration solutions to calculate their results but also to analyse the provided calibration solution to verify the validity of their calibrants. The results submitted in the interlaboratory study were discussed amongst all participants in a technical meeting. Tables 2.10 and 2.11 summarize the results obtained in the interlaboratory study. The evaluation of data from calibration experiments was performed according to ISO 8466-1 linear calibration function (ISO, 1990) and ISO 8466-2 second-order calibration function (ISO, 2001). Data submitted by the participants in the interlaboratory trial were evaluated according to ISO 5725-2 (ISO, 1994). With the exception of one laboratory, all participating

Table 2.10 Summary of the results of the interlaboratory study (non-ISO methods)

Sample	Number of sets	Mean $\pm s_R$ (μg/L)[a]	RSD_R (%)[a]
1	10	5.61 ± 0.38	6.7
2	9	2.79 ± 0.43	15.2
3	10	8.24 ± 2.42	29.4
4	8	9.45 ± 0.89	9.4
5	12	3.94 ± 0.90	23.0

[a] *Note*: s_R is the reproducibility standard deviation and RSD_R (%) is the reproducibility relative standard deviation.

Table 2.11 Summary of the results of the interlaboratory study (non-ISO methods)

Sample	Number of sets	Mean $\pm s_R$ (μg/L)[a]	RSD_R (%)[a]
1	17	5.44 ± 0.23	4.1
2	17	2.49 ± 0.50	19.9
3	16	8.26 ± 1.41	17.1
4	15	8.13 ± 1.17	14.3
5	17	3.93 ± 0.64	16.4

[a] *Note*: s_R is the reproducibility standard deviation and RSD_R (%) is the reproducibility relative standard deviation.

laboratories found results ranging from 9.60 to 10.95 μg/L for the 10 μg/L calibration solution, with a mean of 10.06 μg/L and an interlaboratory standard deviation of 0.30 μg/L (RSD of 3.0 %), which confirmed that the calibration solutions used were of good quality and that possible errors were therefore unlikely to be caused by bias resulting from incorrectly prepared laboratory calibrants.

Calibration functions were calculated according to a linear and a second-order model. Both functions led to RSDs in the same range, except for two laboratories (27 and 29) using non-ISO Carbostyril fluorescence quenching methods (and a linear calibration function). This trial has allowed the introduction of both linear and second order calibration models in the standard ISO/DIS 15061 method (ISO, 2001). The results of some laboratories using non-ISO methods (5, 12, 23 and 27) were not considered to be fit for the purpose because the mean results of at least two of the three spiked samples (samples 2, 3 and 5) led to a recovery lower than 80 % or greater than 120 %, and two of the within laboratory RSDs were greater than 10 % . Data reported from Laboratories 23 (four times), 12 (three times), 5, 25, 26 and 33 (once) were also detected as statistical outliers, following calculations made according to ISO 5725-2 (Table 2.9). (ISO, 1994) The results were considered to be good for this difficult determination. The results obtained using the ISO 15061 IC method (ISO, 2001) indicated that the method is fit for the purpose at the studied levels of bromate concentrations (Table 2.12). However, the results from four laboratories (8, 9, 24 and 31) were not accepted on statistical grounds for the above mentioned reasons. Single statistical outlier results were reported by laboratories 3, 7, 9 and 19. The reproducibility results obtained were used for developing the ISO/DIS 15061 standard (ISO, 2001).

The results obtained for the vast majority of the laboratories carrying out the ISO 15061 IC method were considered to be fit for the purpose. In addition to this method, five alternative methods suitable for trace bromate determinations were also considered, namely on-line IC-ICP-MS, simple on-line column chromatography ICP-MS, IC with chlorpromazine post-column reaction and colorimetric detection, and fluorescence quenching with Carbostyril (with pre-treatment), which are all capable of achieving a bromate detection limit below 1 μg/L. A field method with methylene blue and fluorescence quenching with Carbostyril without sample pre-treatment did not lead to satisfactory results at this level of bromate concentrations.

Table 2.12 Some Bromate results for drinking waters

Sample No.	Sample type/ description	Bromate (μg/L)	Method
1	Non-EC bottled water	26	IC-CD
2	Non-EC bottled water	<0.6	IC-CD
3	Non-EC bottled water	38	IC-CD
4	Non-EC bottled water	<0.6	IC-CD
5	Non-EC bottled water	<0.6	IC-CD
6	Non-EC bottled water	4.9	IC-CD
7	Non-EC bottled water	2.2	IC-CD
8	Non-EC bottled water	<0.6	IC-CD
9	EC bottled water	0.27	FI-ICP-MS
10	EC bottled water	0.21	FI-ICP-MS
11	EC bottled water	0.11	FI-ICP-MS
12	EC bottled water	0.48	FI-ICP-MS
13	EC mineral water	<0.13	FI-ICP-MS
14	EC mineral water	<0.13	FI-ICP-MS
15	EC mineral water	0.85	FI-ICP-MS
16	EC process water	16.0	FI-ICP-MS
17	EC process water	7.4	FI-ICP-MS
18	EC process water	79	FI-ICP-MS
19	Further bottled waters	Mauritius CWM	??
20	Sodium hypochlorite (15 %)	1048 mg/L	FI-ICP-MS
21	Water treated with sodium hypochlorite No. 20	15 μg/L	FI-ICP-MS

2.7 TOXICITY, OCCURRENCE AND CURRENT STATUS OF BROMATE IN DRINKING WATERS

Historically bromate has been associated with water treatment as a by-product of such processes as ozonation. However, through the bromate monitoring programmes now in place, evidence has been found that it can also occur in the environment as a result of industrial pollution (e.g., photographic waste) and can affect raw water sources. An example of this has occurred in the UK where levels of bromate have been found in both public and private water sources. The bromate is very stable in the environment and does not readily degrade. Currently the technology and technical expertise for dealing with this type of environmental pollution is in its infancy, and a significant amount of research and development has been undertaken to understand both the technical treatment solutions and the hydrological behaviour mechanisms that could provide long term management options.

The International Agency for Research on Cancer (IARC) and the US Environmental Protection Agency have evaluated the carcinogenicity of bromate in drinking water. Both IARC and US EPA classified this chemical as B2–probable human carcinogen under its current guidelines (US EPA, 1986; IARC, 1990). The cancer weight

of evidence classification is based on all routes of exposure. Under its 'Proposed Guidelines for Carcinogen Risk Assessment' (US EPA, 1996), the EPA determined that bromate should be evaluated as a likely human carcinogen by the oral route of exposure.

The US EPA has subsequently published a comprehensive toxicological review of bromate (US EPA, 2001). Studies with rats based on low-dose linear extrapolation, using the time-to-tumour analysis, and using the Monte Carlo analysis to sum the cancer potency estimates for kidney renal tubule tumours, mesotheliomas, and thyroid follicular cell tumours, gave an upper-bound cancer potency estimate for bromate ion of 0.70 per mg/kg day. This potency estimate corresponds to a drinking water unit risk of 2×10^{-5} per μg/L, assuming a daily water consumption of 2 litres/day for a 70-kg adult. Lifetime cancer risks of 10^{-4}, 10^{-5}, and 10^{-6} are associated with bromate concentrations of 5, 0.5, and 0.05 μg/L, respectively. A major source of uncertainty in these estimates is from the interspecies extrapolation of risk from rats to humans.

The acute toxic dose of bromate (expressed as bromate) for a 70-kg individual is estimated at about 3 g (Dreisbach and Robertson, 1987). As a typical person will consume 2 litres of tap water per day, this would correspond to a bromate concentration of 1500 mg/L 'acute concentration'. This is 150 000 times higher than the statutory EC drinking water limit concentration of 10 μg/L (Council Directive, 1998), which can be regarded as a chronic toxicity safe limit.

The important precursor to bromate formation in drinking water is bromide. In the United States, the average bromide concentration in drinking water is estimated to be approximately 100 μg/L (AWWARF, 1997). Only 6.3 μg/L of bromide needs to be quantitatively converted to bromate upon ozonation to exceed the drinking water directive limit of 10 μg/L bromate. Some natural sources of bromine in groundwater are saltwater intrusion and bromide dissolution from sedimentary rocks. Bromate in drinking water is mainly formed from the oxidation of naturally occurring bromide ions. Thus any oxidation process in the presence of a significant concentration of bromide ions can contribute to the formation of bromate (e.g., ozonation of a water containing bromide ions or electrolysis of sodium chloride containing bromide ions in the production of sodium hypochlorite) (Legube *et al.*, 2004). About seven years ago, a sample of sodium hypochlorite that was marketed for water disinfection was submitted to one of the authors (KCT). It contained over 1000 mg/L bromate. Water companies have instituted strict controls over supplied chemicals that are used in water treatment/disinfection processes to ensure absence of significant amounts of bromate and bromide. Table 2.12 gives bromate results for some bottled waters, many of which were found to contain significant levels of bromate. One of the bottled waters listed in Table 2.12 (Sample 3) was previously analysed a few years ago and found to contain 120 μg/L of bromate. All the waters containing bromate were thought to contain bromide derived from seawater intrusion into the ground water aquifer and were subjected to ozonation as a disinfection process. A few years ago, the Coca-Cola soft drinks company, in an attempt to explore the drinking water market, launched a treated bottled water product in the UK under a brand name Dasani. Taste improver calcium chloride containing bromide was added during

the treatment process prior to ozonation, thus contributing to bromate formation. Bromate levels as high as 22μg/L were reported in these waters and the product was immediately was removed from the market (*The Guardian*, 2004). The results in Table 2.12 demonstrate the importance of monitoring for bromate in bottled and tap waters whenever ozonation is employed in the water treatment process. Chemicals used in water treatment should also be subjected to bromide and bromate monitoring.

As bromate is stable once generated, attention is being paid to effluents and wastewaters treated by ozonation. Bromide-containing effluents will contribute to the rise of bromate levels in receiving water bodies which are subsequently used as a source for drinking waters. This calls for essential regulation of bromide and bromate in effluents and wastewaters prior to final discharge.

For bromate analysis, ethylenediamine (EDA) is added to the sample in order to convert any hypobromite present into the corresponding bromamines, thus preventing ongoing conversion to bromate. Bromate has been found to be stable in a range of drinking waters over three months using amber glass bottles either with or without EDA (Thompson, 1999).

REFERENCES

Achilli, M. and Romele, L. 1999. *J. Chromatog. A*, **847**, 271–277.

American Water Works Association Research Foundation (1997) Formation and control of brominated ozone by-products. *AWWARF Report* No. 90714.

Charles, L., Pepin, D. and Casetta, B. 1996. *Anal. Chem.*, **68**, 2254.

Council Directive 98/83/EC. 1998. (November 1998), *Official Journal of the European Communities*, **41**, Part 330, 32–54.

Creed, J.T., Magnuson, M.I., Pfaff, J.D. and Brockhoff, C. 1996. *J. Chromatogr. A*, **357**, 74.

Delcomyn, C.A., Weiberg, H.S. and Singer, P.C. 2001. *J. Chromatog. A*, **920**, 213–319.

Diemer, J. and Heumann, K.G. 1997. *Fresenius J. Anal. Chem*., **357**, 74.

Dreisbach, R. H. and Robertson, W. O. 1987, *Handbook of Poisoning*, Twelfth edition, Appleton and Lange.

Echigo S., Minear R., Yamada H. and Jackson P. 2001. *J. Chromatog. A*, **920**, 205–211.

Elwaer A.E., McLeod C.W., Thompson K.C. and Wiederin D. 1996. *Plasma Source Mass Spectrometry: Developments and Applications*, Royal Society of Chemistry, London, p. 124.

Elwaer A.R. 1999 PhD Thesis, University of Sheffield, UK, Chemistry Department, Elwaer A.R., McLeod C.W. and Thompson K.C. 2000. *Anal. Chem.*, **72**, 5725–5730.

Farrell, S., Joa, J.F. and Pacey, G.E. 1995. *Anal. Chim. Acta*, **313**, 121.

Fletcher I.J. and Hemmings P. 1985. *Analyst*, **110**, 695.

Gahr A., Huber N. and Niessner R. 1998. *Mikrochim. Acta*, **128**, 281.

Gordon, G., Zoshino, K., Themelis, D.G., Wood, D. and Pacey, G.E. 1989. *Anal. Chim. Acta*, **24** 383.

Gordon, G., Bubnis, B., Sweetin, D. and Kuo, C. 1994. *Ozone Sci. Eng*., **16**, 79.

Guinamant, J.-L., Ingrand, V., Muller, M.C., Noij, Th.H.M., Brandt, A., Bruchet, A., Brosse, C., McLeod, C., Sacher, F., Thompson, K.C., de Swaef, G., Croué, J.P. and Quevauviller, Ph. 2000. Laboratory and field methods for determination of bromate in drinking water, *EUR Report*, EN 19601, European Commission, Brussels, 178, pp.

Hautman, D.P., Munch, D.J., Frebis, C., Wagner, H.P. and Pepich, B.V. 2001. *J. Chromatog. A*, **920**, 221–229.

Ingrand, V., Guinamant, J.-L., Bruchet, A., Brosse, C., Noij, Th.H.M., Brandt, A., Sacher, F., McLeod, C., Elwaer, A.R., Croué, J.P. and Quevauviller, Ph. 2002. Determination of bromate in drinking water: development of laboratory and field methods, *Trends Anal. Chem.*, **21**, 356–365.

International Standards Organization 1990. Water quality – Calibration and evaluation of analytical methods and estimation of performance characteristics, Part 1: Statistical evaluation of the linear calibration function. ISO 8466-1.

International Standards Organization 1994. Accuracy (trueness and precision) of measurement methods and results, Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method. ISO 5725-2.

International Standards Organization 2001a. Water quality – Calibration and evaluation of analytical methods and estimation of performance characteristics, Part 2: Calibration strategy for non-linear second-order calibration functions. ISO 8466-2.

International Standards Organization 2001b. Water quality – Determination of dissolved bromate: Method by liquid chromatography of ions. ISO/DIS 15061.

IARC, 1990. *Monographs on the Evaluation of Carcinogenic Risks to Humans*, WHO: Geneva, 1990.

Kurokawa, Y., Maekawa, A. and Takahashi, M. 1990. Toxicity and carcinogenicity of potassium bromate – a new renal carcinogen. *Environ. Health Perspect.* **87**, 309–335.

Legube, B., Parinet, B., Gelinet, K., Berne F. and Croue J. 2004. *Water Research*, **38**, 2185–2195.

Liu, Y., Mou, S. and Heberling S. 2002. *J. Chromatog. A*, **956**, 85–91.

Liu Y. and Mou S. 2004. *Chemosphere*, **55**, 1253–1258.

Quevauviller, P. 1997. EC Workshop on Reference Materials for the Quality Control of Water Analysis, Lisbon, Portugal, June 18–19, 1997.

Mena, M. L. and McLeod, C. W. 1996. *Mikrochim. Acta*, **123**, 103.

Mena, M. L., Morales, A., Cox, A. G., McLeod, C. W. and Quevauviller, P. 1995. *Quim. Anal.*, **14**, 164.

Sanz-Medel, A. (ed.) 1999. *Flow Analysis with Atomic Spectrometric Detectors*, Elsevier.

The Guardian, 2004. March 20.

Thompson, K. C. 1999 Report on the stability of bromate in potable waters and on the interlaboratory trial to test various bromate analysis methods for potable waters. *Contract No SMT4-CT-97-2-2134*, December. (CR258).

US Environmental Protection Agency, 1986. Guidelines for carcinogen risk assessment. Federal Regulation 51(185):33992–34003.

US Environmental Protection Agency, 1991. *EPA Method 300.0*, EPA/600/R93/100.

US Environmental Protection Agency, 1996. Proposed guidelines for carcinogen risk assessment. Federal Regulation 61(79):17960–18011.

US Environmental Protection Agency, 1997. *EPA Method 300.1*, EPA/600/R98/188.

US Environmental Protection Agency, 2001. Toxicological review of bromate, in support of summary information on the integrated risk information system (IRIS), March 2001. CAS No 15541-45-4.

Valcarcel, M. and Luque de Castro, M.D. 1991. *Non-chromatographic Continuous Separation Techniques*, Royal Society of Chemistry, London.

Weinberg, H.S., Delmyn, C.A. and Unnam, V. 2003. *Environ. Sci. Technol.* **37**, 3104–3110.

Wolfis, G. and Brandt, A. 1997. Ontwikkeling van een bepalingsmethode voor bromate in water, SWI 96.213, Nieuwegein.

World Health Organization, 1991. *Revision of the WHO Guidelines for Drinking Water Quality*, WHO, Geneva.

3
Lead Monitoring

Theo van den Hoven and **Nellie Slaats**

Analytical Methods for Drinking Water: Advances in Sampling and Analysis Edited by P. Quevauviller and K. C. Thompson © 2006 John Wiley & Sons, Ltd. ISBN: 0-470-09491-5

3.1 FACTORS DETERMINING THE LEAD CONCENTRATION IN DRINKING WATER

3.1.1 Sources of Lead in Drinking Water

Lead pipes

Lead pipes are the major source of lead in drinking water. In the past, lead pipes were considered to be a convenient and suitable material for the conveyance of water. Lead is easily formed, cut and jointed, and its flexibility provides resistance to subsidence and frost. The thickness of lead pipe and its resistance to pitting corrosion also made it a desirable and durable material.

In most countries lead pipes are forbidden nowadays and lead pipes are only found in old houses. Lead pipes are encountered almost exclusively in the service pipe and internal plumbing systems.

Plumbing materials

Whilst lead pipes are the main source of high lead concentrations, lead concentrations higher than 10 μg/l can also be observed for properties without any lead pipes. Lead-based solders (for copper plumbing), copper alloys (brasses and bronzes) used mainly for fittings, galvanized steel pipes and uPVC (when stabilized with lead salts) can release lead into drinking water.

Lead based solders (tin/lead solders) contain up to 60 % of lead, which can be released into water through galvanic corrosion. The corrosion rate is increased by high concentrations of chloride and nitrate but is inhibited by sulfate, silicate and orthophosphate. Lead concentrations at the tap depend not only on the corrosion rate but also on the number of leaded joints in the plumbing, the area of solder exposed to water at each joint, and the water usage pattern (Gregory, 1990).

Experiments on the leaching of lead from copper alloy (brasses and bronzes) fittings suggest that lead is prone to be concentrated on the internal surface during machining, leading to the possibility of elevated lead concentrations from new

fittings. There is no obvious correlation between the lead content of the alloy (normally between 2.25 % and 5 %) and the tendency for lead to leach.

The zinc lining of galvanized steel pipes can contain up to 1 % lead, whereas steel itself contains much less lead (0.0005 to 0.01 %) (Leroy, 1993). Leaching of lead from galvanized steel depends strongly on the corrosion rate of the material. Zinc lining can be subject to galvanic corrosion, especially in high conductivity waters. This process is also strongly dependent on pH (galvanized steel should not be used for water of a pH under 7.3) and is accelerated by contact with copper materials and high temperatures, as in hot water systems (Wagner, 1992). Orthophosphate and silicate have been demonstrated to be effective at controlling zinc corrosion.

Experience in France shows that lead concentrations from galvanized steel plumbing are normally in the range of <1 to 10 μg/l. However, values between 10 and 25 μg/l can be observed quite frequently. Higher values (up to 100 μg/l or more) are exceptional but only in association with high corrosion of the material, and high iron and zinc concentrations (red waters).

PVC pipes

Unplasticized polyvinyl chloride (uPVC) is a commonly used material for mains and domestic potable water piping. The additives used in uPVC include heat stabilizers to reduce decomposition of the uPVC during manufacture. Stabilizers are often lead salts. It has been shown that leaching of lead can occur, but this seems to be significant only for new uPVC pipes (Packham, 1971; Poels and Dibbets, 1982). In some countries (e.g. France) the application of lead salts as stabilizers is not allowed.

3.1.2 Factors Determining the Lead Concentration in Drinking Water

Lead concentrations at the consumers' tap are mainly determined by the following factors:

- consumer behaviour (e.g. water use pattern, mean inter-use stagnation time);
- water composition (e.g. pH, hardness, orthophosphate (o-PO_4) dosing);
- plumbing materials and dimensions.

Consumer behaviour

The *water use pattern* has a major influence on the stagnation time and lead release and thus on lead concentration (e.g. Bailey *et al.*, 1986a). More specifically, the

following parameters are of major influence:

- mean inter-use time;
- volume of water drawn;
- flow rate.

Mean inter-use time

WRc performed a detailed study and a statistical assessment of water use in the United Kingdom in relation to the problem of lead monitoring at the consumer's tap (Bailey *et al.*, 1986b). The study covered 100 households in 22 districts in England, Scotland and Wales. The consumption of water, with distinction between potable and non-potable use, and time of use, was recorded for each household during one week. The results of the study are summarized in Table 3.1.

As can be seen in Table 3.1, the mean inter-use stagnation time decreases with increasing numbers of occupants. On average, the inter-use stagnation time is about 30 minutes. This value is in accordance with data observed in independent studies in Germany, France and The Netherlands. The study in France refers to experiments where 30-minute stagnation time samples gave results comparable with composite proportional samples (Randon, 1996). Results from The Netherlands show that composite proportional samples corresponded to 30 minutes' stagnation time in the stagnation curve derived from the lead pipe test (Van den Hoven, 1986). Data from Germany refer to experiments where the average inter-use time has been measured directly, clearly showing the wide spread in mean inter-use stagnation times that can be observed in different households. As lead concentrations rise rapidly in this range of stagnation times, it can be concluded that lead concentrations might vary strongly between households.

Volume of water drawn

The volume of water drawn affects the contact time of the water with plumbing materials and as a result, the amount of metals leaching out of these. In addition, in mixed plumbing systems the volume of water drawn determines which materials affect the

Table 3.1 Inter-use stagnation times for different household sizes (Bailey *et al.*, 1986b)

Household size (persons)	Mean[a] (min)	Standard deviation (min)
1	47	23
2	29	14
3	24	13
4	22	13
5+	18	6

[a] Mean inter-use stagnation time: time between draw for dietetic purposes and the previous draw.

water quality. Therefore, the volume of water drawn affects lead concentrations. On average the volume of water drawn from a tap is 1.2 litres.

Flow rate

Research has shown that the flushing regime for lead pipes has a considerable effect on the lead concentration (Vewin, 1987). If the flow in the pipes is turbulent ($Re >$ 2300) the lead concentration is higher than after flushing with laminar flow. This is probably due to the release of particulate lead. In practice, consumers draw water with an average flow rate of 5 litres/minute, which corresponds to turbulent flow (in pipes of 19 mm diameter, $Re > 5000$).

Water composition

In the case of lead pipes, simple oxidative corrosion of the metal forms a coating of lead carbonate on the inside wall of the pipe. As shown in theoretical and empirical studies, the lead solubility (maximum lead concentration) is a function of water characteristics, mainly pH, alkalinity and temperature, as well as, eventually, orthophosphate concentration (Sheiham and Jackson, 1981; Kuch and Wagner, 1983: Van den Hoven, 1986; Schock, 1989,1990,1994; Wagner, 1992; Leroy, 1993). For a given alkalinity, lead solubility decreases when pH increases. Theoretical lead solubility varies between several mg/l for very soft waters with low pH (alkalinity < 30 mg/l $CaCO_3$ and pH < 6.5) to less than 100 μg/l in waters with alkalinity between 50 and 150 mg/l $CaCO_3$ and pH above 8.

Plumbing dimensions and design

The effect of the dimensions (length and diameter) of lead pipes and other characteristics of domestic plumbing can influence the dissolution of lead:

- the influence of stagnation time on lead concentration varies with pipe diameter. For lead pipes, experimental stagnation curves show that the maximum lead concentration is reached after about 5 to 6 hours for pipes of 10 mm internal diameter but only after several tens of hours for pipes of 50 mm diameter (Kuch and Wagner, 1983). Mass transfer models have been developed for calculating lead concentration for a given stagnation time and equilibrium lead solubility, knowing the lead pipe length and diameter (Kuch and Wagner ,1983; Van den Hoven, 1987);

- the mean inter-use stagnation time is influenced by the configuration of the plumbing system, in particular by the location of the sampling point in the house (relative to other taps, washing machine, toilets, etc.). The situation can be very different between an isolated house and a flat in a collective building;

- when lead is coupled to a dissimilar metal (e.g. copper), galvanic corrosion can occur at a much faster rate, releasing soluble and insoluble corrosion products into the water (Britton and Richards, 1981);

- the environment (room temperature, vibrations, etc.) of lead pipes can also have an impact on lead concentration. Vibrations can be caused by traffic, but also by elevators in apartment buildings or by water hammer in the plumbing system.

3.2 SAMPLING OF LEAD IN DRINKING WATER

3.2.1 Available Sampling Procedures

Sampling of lead in drinking water has to include contributions from all sources and factors influencing the lead concentrations at the tap. Therefore, various sampling techniques with different purposes have been developed and routinely applied. These are listed in the next section.

Tap samples

(i) *Composite proportional (COMP)*: A consumer operated device is fitted to the drinking-water tap, which splits off a small constant proportion (±5 %) of every volume of water drawn for dietetic purposes (during one week);

(ii) *Fully flushed (FF)*: A sample is taken after prolonged flushing of the tap after flushing at least three plumbing volumes;

(iii) *Random daytime (RDT)*: During office hours a sampler visits a property at a random time (the choice of the property may also be randomized). A single sample, typically 1 litre, is taken from a drinking water tap without flushing any water from the tap beforehand;

(iv) *Fixed stagnation time*: After prolonged flushing of the tap, water is allowed to stand in the plumbing system for a defined period after which a sample is taken without flushing the pipe beforehand. A typical fixed stagnation time is 30 minutes (30MS).

(v) *First draw*: A sample is taken from the drinking water tap in the morning before water has been used anywhere in the house and without flushing the tap beforehand.

Supply area lead level

The lead-pipe test is used to assess the lead level at the consumer's tap. Basically, the lead-pipe test measures the lead concentration in aged lead pipes for selected

periods of stagnation. From the stagnation curve the average lead concentration of tap water can be estimated (Van den Hoven, 1987). The lead-pipe test is internationally recognized as being a very useful instrument in determining the effects of remedial actions in decreasing lead solubility in drinking water. In The Netherlands, the government accepts the lead-pipe test for compliance monitoring.

3.2.2 Definition of a 'Representative Sample'

In the Drinking Water Directive 98/83/EC, the parametric value (PV) for lead is 10 μg/l. The parametric value refers to water as it emerges from the customer tap, assessed on the basis of 'representative' monitoring (Note 3). Note 3 is as follows:

> *The values apply to a sample of water intended for human consumption obtained by an adequate sampling method at the tap and taken so as to be representative of a weekly average value ingested by consumers. Where appropriate the sampling and monitoring methods must be applied in a harmonized fashion to be drawn up in accordance with Article 7(4). Member States must take account of the occurrence of peak levels that may cause adverse effects on human health.*

Variations in average weekly lead concentrations at the consumers' tap

The average weekly intake of lead via drinking water is determined by water composition, plumbing system and consumer behaviour. These factors vary considerably, not only between supply zones, properties and individual consumers, but also over time.

The water composition in general varies slowly (seasonally). Although the plumbing system hardly changes over a long period, the influence of vibrations (e.g. by traffic) on the release of lead from service pipes may vary in relatively short periods. These factors determine the pattern of build-up of lead concentration in water inside a lead pipe over time (i.e. the stagnation curve) and the equilibrium lead concentration (saturation or plateau value). Figure 3.1 shows an example of the influence of water characteristics on the stagnation curve.

The water consumption pattern of an individual consumer changes not only seasonally (due to temperature or holidays) but may also vary from day to day, depending, for example, on the number of people at home (including visitors). Furthermore, considerable differences in mean inter-use time between households exist. Therefore, the average weekly intake of lead via drinking water by the individual consumer may vary considerably throughout time. This is illustrated in Figure 3.2, which shows the upper lead stagnation curve of Figure 3.1 between 0 and 90 minutes, being the range of mean inter-use stagnation times typically found.

As shown, a variation of 10 minutes in mean inter-use stagnation time, which is quite normal (Bailey found standard deviations up to 22 minutes, depending on household size), has considerable influence on the average weekly intake of lead via drinking water. Furthermore, this figure shows that by lowering the mean

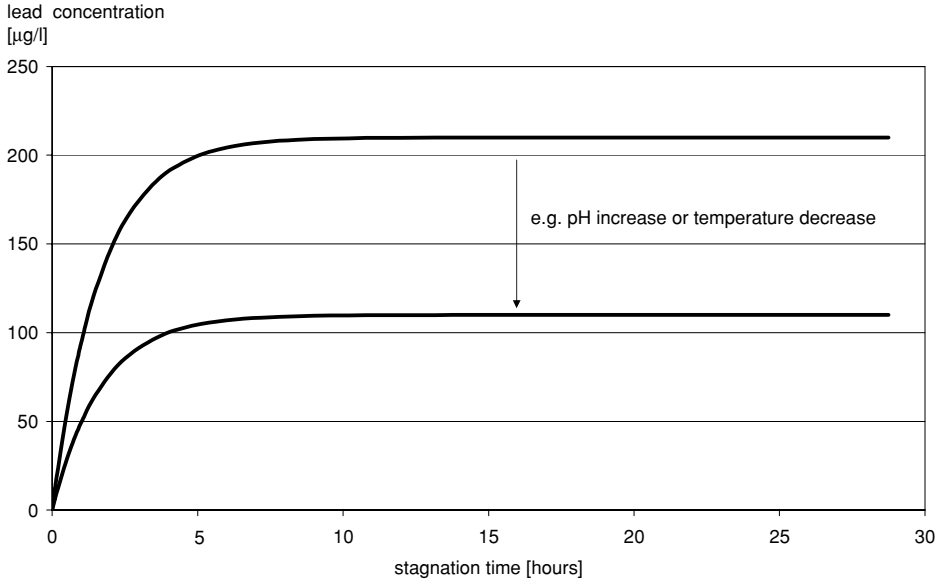


Figure 3.1 Influence of water characteristics on the stagnation curve

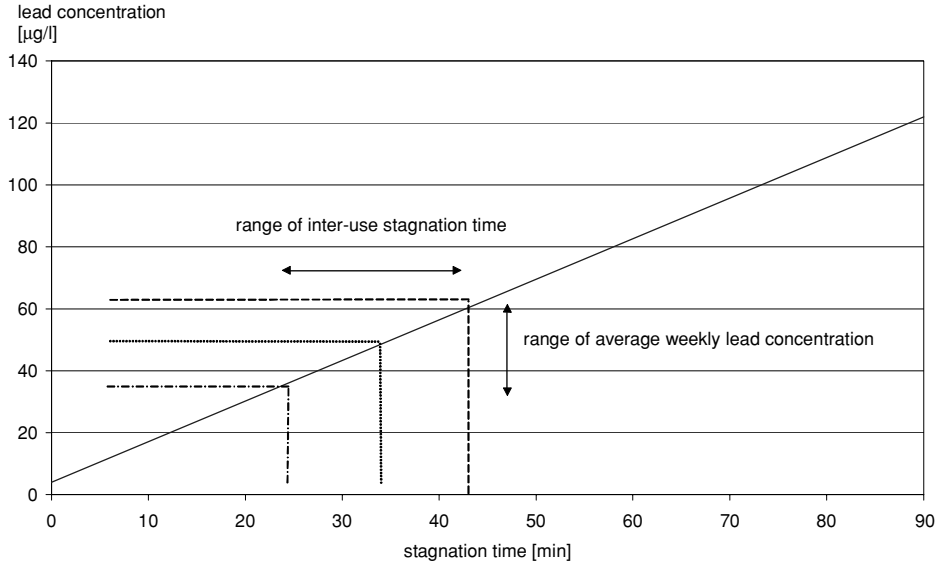


Figure 3.2 Influence of variations in inter-use stagnation time on average weekly lead concentration

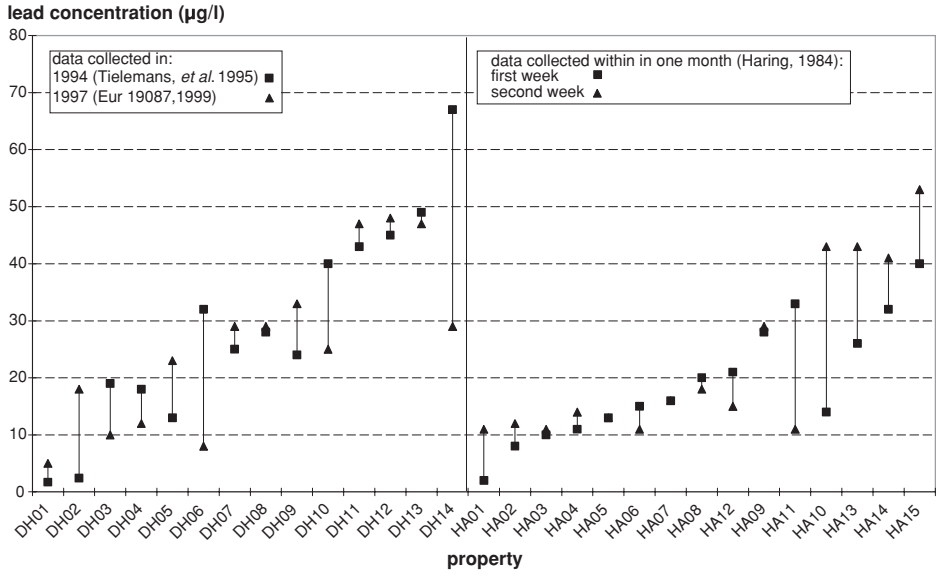


Figure 3.3 Results of duplicate composite proportional samples, showing variations in some properties resulting from variations in consumer behaviour

inter-use stagnation time by flushing before consumption, the average weekly lead concentration can effectively be lowered.

Strong variations in weekly average intake are indeed observed in practice, as can be concluded from two separate studies. One study refers to 15 individual properties (in one supply zone), that were each sampled twice within one month, so the variations in the factors determining the average weekly lead concentration should be small (Haring, 1984). The right hand side of Figure 3.3 gives the results of the first and second composite proportional sample for each property.

The second study refers to 14 individual properties (in one supply zone) that were sampled (composite proportional sampling) in a study in 1994, and were sampled again in the lead monitoring study (Tielemans *et al.*, 1995; EUR19087, 1999). In these properties the plumbing system and household situation were the same and there was no significant change in water quality. The left hand side of Figure 3.3 gives the results of the first and second sample for each property. As can be seen in Figure 3.3, the average weekly concentration of lead in drinking water varies considerably from week to week in some properties, even if two samples are taken one shortly after the other. In about half the properties in each study the concentration is lowest in the first week, in the other half in the second week. This shows that the difference between the two samples in one property cannot be accounted for by water quality change. As the plumbing system remained unchanged, the variation in lead concentration has to be accounted for by variation in consumer behaviour.

Variations of average weekly lead concentrations in a supply zone

At supply zone level, where the water quality may be considered as being approximately uniform, the variation in plumbing systems (both materials and design) and the diversity of household types determines the range of lead levels found at the consumers' tap. In The Netherlands, the average weekly lead concentration, as assessed with composite proportional sampling, was determined in 17 supply zones in the period 1979–1980. In each zone about 50 properties were sampled. Figure 3.4 shows the range of lead concentrations and the median concentration in each of the 17 supply zones. As indicated in this figure, the range of lead concentrations, as determined by proportional sampling, varies widely in some supply zones. For example, in supply zones 4 to 6 the median concentration is well below 10 μg/l, but an individual consumer may still be exposed to an average weekly intake of more than 50 μg/l. On a supply zone level it is therefore necessary to select properties and households representative for that area.

Number of samples

The number of samples needed to get an accurate estimate of the average weekly intake in an area depends on the range of variation of lead levels found in that area and the true level of noncompliance in that area (i.e. the percentage of all properties

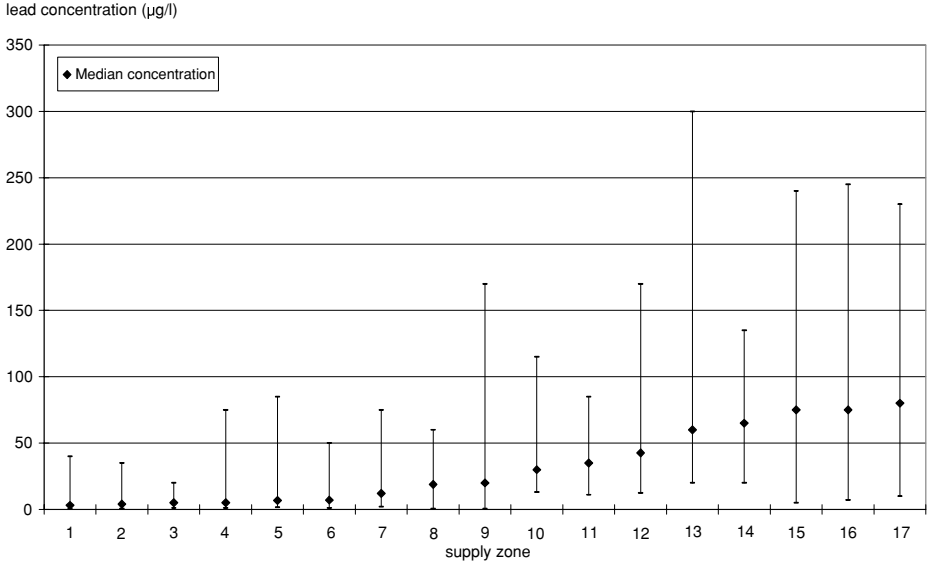


Figure 3.4 Range of lead concentrations found in 17 supply zones in The Netherlands (Haring, 1984)

where lead exceeds the PV). Especially in supply zones with a variation in plumbing systems, the sampling frequency for audit monitoring (DWD98/83/EC, Table B1, Annex II, Common Position) of one sample per year for 50 000 inhabitants is too low to detect the level of excess of the parametric value. If, for instance, the percentage of true noncompliance in an area is 10 %, at least 59 samples from randomly chosen properties are needed to have a 95 % probability of detecting the excess. The number of samples needed increases as the true level of noncompliance decreases (Baggelaar and Van Beek, 1995). The number of samples needed is independent of the size of the supply zone (number of properties) and the sampling procedure used.

Depending on the local situation, the number of samples should be increased, or target monitoring (sampling in properties with lead plumbing or performing lead pipe tests) can be applied in addition to the required audit monitoring. In this way water authorities can take into account the worst case situation (the maximum average weekly intake of lead through drinking water) that might occur in a supply zone.

3.2.3 Representative Sampling at an Individual Consumer's Tap

The composite proportional sample (COMP) procedure is a method that actually aims to collect samples of each draw of water used for dietetic purposes at the monitored tap. This is, therefore, the only procedure that takes into account all variations within one week. Thus, the composite proportional sample should be considered to be the only really representative sample, i.e. representative for the average weekly intake of the consumers sharing the tested tap during the test week.

The composite proportional sample is taken with a consumer operated device fitted to the drinking water tap, which splits off a small constant proportion ($\approx$5 %) of every volume of water drawn for dietetic purposes during one week. Figure 3.5 gives a schematic view of a proportional sampling device.

The composite proportional sampling device was developed in the 1970s. In itself, the composite proportional sampling procedure is a long-term test, which is not appropriate for large scale and routine monitoring. Therefore, short-term sampling procedures were developed to give an accurate estimate of the average weekly intake of lead via drinking water, as established with the composite proportional sample.

3.2.4 Lead Analyses in Tap Water

Requirements

With the aim of complying with the parametric value for lead of 10 μg/l, it is important to have satisfactory analytical methods for the detection of lead in drinking water. These methods need to be reviewed on the basis of requirements for the trueness and precision in measuring lead concentrations. Laboratories are allowed to use their

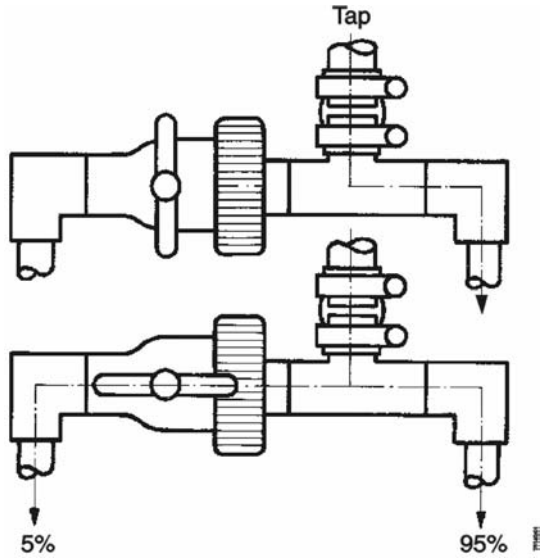


Figure 3.5 Proportional sampling device. A hose connects the split-off valve and the sample collection bottle, and the discharge of the sample hose should at all times be above water level in the sample bottle, and the air should be able to escape from the sample bottle. In most cases, a 3-litre sample bottle is sufficient for 1 week. A sampler or the consumer has to check that the sample bottle does not overflow and, if necessary, replace the sample bottle with an empty one

own methods, but the results have to be comparable. Table 3.2 gives an overview of the limit, trueness, precision and limit of detection of lead as stated in the DWD.

Sampling and pre-treatment

High variability can be found in the results of lead analyses. This is partly due to limited trueness and precision of analytical methods. Variability in the results of lead analyses also stems from the different pre-treatment methods that are used.

Table 3.2 Required accuracy of lead detection in drinking water

	Limit ($\mu g\ l^{-1}$)	Trueness[a] ($\mu g\ l^{-1}$)	Precision[b] ($\mu g\ l^{-1}$)	LoD[c] ($\mu g\ l^{-1}$)	Guideline WHO ($\mu g\ l^{-1}$)
Lead Pb	10	1	1	1	10

[a] The closeness of agreement between the average value obtained from a large series of test results and an accepted reference value (ISO 5725-1).

[b] The closeness of agreement between independent test results obtained under stipulated conditions (ISO 5725-1). The precision is computed as the standard deviation.

[c] Limit of detection is either three times within standard deviation of a natural sample containing a low concentration of the compound, or five times the within standard deviation of a blank sample.

Pre-treatment of the sample is especially important if lead particles are present in the sample. To obtain representative results, prescription of representative, reproducible, precise and accurate sampling, pre-treatment and methods of analysis are essential in the sampling procedure.

Analytical techniques

For the determination of lead concentrations in drinking water, the analytical methods are atomic absorption spectrometry – electro-thermal atomization (AAS-ETA or AAS-furnace), inductively coupled plasma with detection by atomic emission spectrometry (ICP-AES) or detection by mass spectrometry (ICP-MS). Laboratories are free to use their own chosen analytical techniques. More attention will be required to achieve the necessary analytical accuracy at the lower limit for lead.

3.3 COMPARISON OF SAMPLING PROCEDURES IN THE FIELD

3.3.1 European Study

The lead sampling procedures described in Section 3.2 were evaluated in a European broad study (EUR19087, 1999). The results of this study are described in this section.

3.3.2 Applied Sampling Procedures

On the basis of the experiences described in Section 3.2, the following sampling procedures were selected for the field experiments:

- composite proportional (COMP) as the reference method;
- 30-minute stagnation time (30MS);
- random daytime (RDT);
- fully flushed (FF).

The 30-minute stagnation time (30MS) was chosen, as it represents the average inter-use stagnation time. Random daytime and fully flushed were added because of their practicality and cost effectiveness. Also, random daytime, when taken during office hours, might be in the range of the average inter-use time. Other sampling methods are very unlikely to give representative results.

For the 30-minute stagnation time procedure, as the internal plumbing system is flushed with three pipe volumes of water before the 30 minutes' stagnation, in a

mixed plumbing system (e.g. lead plumbing with copper connection to sampled tap) the water in a 1-litre 30MS sample will have had only limited contact with lead and will therefore have a relatively low lead content. If a larger sample is taken, the lead content will be higher. Therefore, two consecutive 1-litre samples (30MS1, 30MS2) were taken after the stagnation period.

For RDT the best approach seems to be to stay close to the average draw volume, therefore a sample volume of 1 litre was chosen. The sample volume has no effect on the lead content of the FF sample, so a 1-litre sample was chosen.

Although the procedures have already been described in Section 3.2.1, the sampling procedures are clarified below for evaluation in the field test.

Composite proportional (COMP) sample

A consumer-operated device, attached to the tap, collects the composite proportional sample. The composite proportional sampling device is connected to the kitchen tap through a coupling nut or a hose clip. In practice, this might cause problems, as some taps are shaped in a way that makes it very difficult to attach the sampling device (e.g. mixer and spray-type taps). The gap between device and tap should be as short as possible. The device should be connected horizontally.

A hose connects the split-off valve and the sample collection bottle. The hose should go down at least 15 centimetres before bending off horizontally. The discharge from the sample hose should at all times be above the water level in the sample bottle. The air should be able to escape from the sample bottle. In most cases, a 3-litre sample bottle is sufficient for 1 week. A sampler or the consumer has to check that the sample bottle does not overflow and, if necessary, replace the sample bottle with an empty one.

When water for consumption (drinking or cooking) is drawn, the split-off valve should be turned horizontally, thus directing 5 % of the drawn volume to the sample bottle. The valve should be turned vertically when water is drawn for purposes other than consumption (e.g. cleaning, washing hands).

Random daytime sample

The random daytime sample (RDT) has to be taken at a random time during office hours, avoiding the periods of frequent water use (breakfast, lunch and dinner) and the period of overnight stagnation. A professional sampler collects a 1-litre sample, without flushing the tap.

> *NOTE: A sample taken by the consumer cannot be considered a true random daytime sample, as the consumer is likely to take a sample with extreme stagnation time (either a first draw sample or a fully flushed sample).*

Fully flushed sample

The sampler has to estimate the plumbing system volume. The fully flushed (FF) sample is taken after flushing three pipe volumes or 5 minutes (if the plumbing dimensions are not known) at 5 litres/minute. The sampler collects a 1-litre sample.

Thirty minutes' stagnation time

After flushing the system as described before, the water is allowed to stand for 30 minutes. The sampler has to make sure that no water is used from the internal plumbing system during the stagnation period (including alternative taps, toilets and washing machines, as well as the tap that is being sampled). After exactly 30 minutes the first litre (30MS1) and the second litre (30MS2) are drawn.

3.3.3 Characteristics of Test Areas

Test areas have been selected on the basis of:

- water composition (e.g. plumbosolvency, hardness, o-PO_4 dosing);
- plumbing materials;
- willingness of water companies and consumers to cooperate.

Although there are numerous different water types to be considered, for the purpose of validation of the protocol the actual lead concentration found in a test area is the most important factor. Three types of area can be distinguished, namely areas with low, medium and high plumbosolvency. A number of properties with comparable water quality (not necessarily the same supply area) is considered as one area. Per area about 30 properties were selected.

With regard to plumbing, the pipe material is the most important factor. Difference is made between lead plumbing and other materials (copper, galvanized steel and plastics). About 50 % of properties selected in each test area should have lead plumbing. Furthermore, the length of the plumbing system will be taken into account. Two categories have been established: less than 20 metres to tap (houses) and more than 30 metres to tap (apartments). Table 3.3 lists the main characteristics of the test areas.

The field tests were performed in eleven areas. The samples from each area were analysed by national laboratories that had proved capable of meeting the demands on analytical capabilities (Section 3.2.4).

Table 3.3 Test-area characteristics

Area	Water composition plumbosolvency	pH range	Remarks
A	low	7.0–7.5	300 mg/l $CaCO_3$ + o-PO_4
B	high	6.9–8.9	200 mg/l $CaCO_3$ upland
C	medium	7.3–7.8	200∼250 mg/l $CaCO_3$
D	medium	7.0–8.4	
E	low	7.1–8.9	
F	medium	8.3–8.8	Softened by pellet softening
G	high	7.6–8.4	
H	high	7.1–7.9	
I	medium	8.1–8.4	
J	medium	7.4	
K	low	7.3–8.3	Mix of different water types, partly + o-PO_4

3.3.4 Applied Test Procedures

Figure 3.6 schematically represents the sampling programme performed in each property. As can be seen, the test period in each property was 1 week. On day 0 the composite proportional sampling device was installed, samples were taken (RDT, FF, 30MS1, 30MS2) and the questionnaire was filled out. This questionnaire includes property information (e.g. plumbing type, pipe length, occupants, etc.).

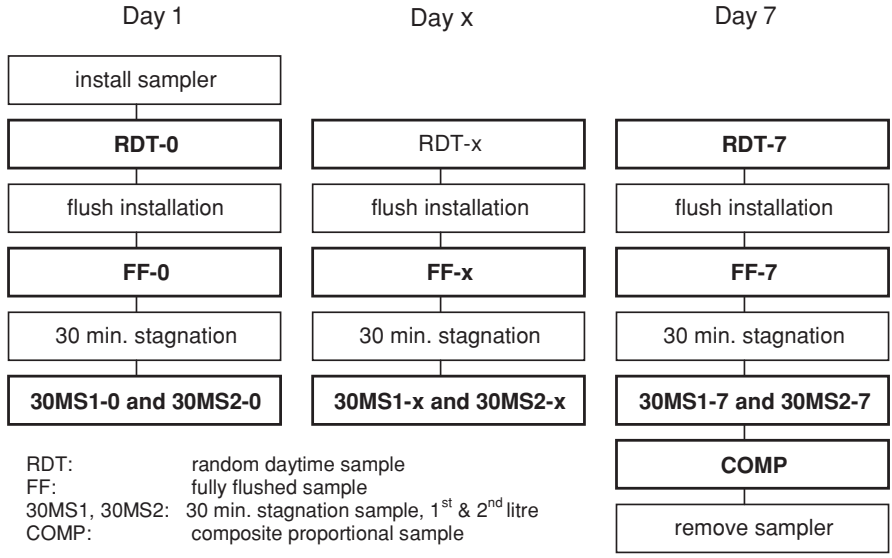


Figure 3.6 Sampling programme

In the middle of the test period (day *x*) samples (RDT, FF, 30MS1, 30MS2) were taken and the sampling device was checked. On day 7 samples were taken (RDT, FF, 30MS1, 30MS2), the COMP sample was collected and the sampling device was removed.

3.3.5 Performance Criteria of Sampling Protocols

Based on the four sample types (RDT, FF, 30MS1 and 30MS2), six sampling procedures were evaluated:

- RDT: random daytime sample;
- FF: fully flushed sample:
- 30MS1: first litre of the 30-minute stagnation sample;
- 30MS2: second litre of the 30-minute stagnation sample;
- 30MSA: the average of first and second litre 30-minute stagnation sample (equals the concentration of a 2-litre, 30-minute stagnation sample);
- av(RDT,FF): the average of the RDT and FF sample taken on the same visit.

The performance of the six procedures is judged on the basis of the following criteria:

- representativeness;
- reproducibility;
- costs, practicality and consumer acceptance.

The sampling methods were evaluated against the composite proportional sample. The composite proportional sample was the only sample type that covered all factors influencing the average weekly intake of the consumer: water quality, plumbing materials, network design and consumer behaviour. As the sample was taken during one week, it was representative for that week only. Results might differ from week to week as a result of changes in water use pattern and water quality. If all factors determining the lead concentration at the tap are constant, the composite proportional sample will give the same result.

By definition, the proportional sampling procedure scores 100 % for the criteria of representativeness and reproducibility. However, this applies only when consumers operate the proportional device correctly. To test whether the consumer has used the device correctly, the volume of the composite proportional sample can be checked. In some test areas the volume of the composite proportional sample was noted and used to calculate the average daily water consumption per person. Figure 3.7 shows the water consumption distribution for these test areas, and Figure 3.8 shows the

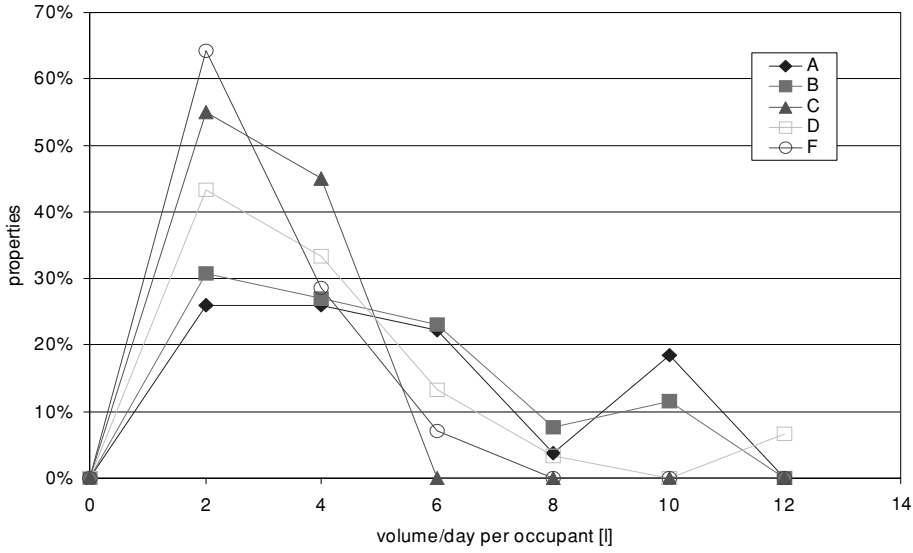


Figure 3.7 Water consumption distribution based on composite proportional sampling

relationship between the mean daily consumption per occupant and the household size.

Figure 3.7 shows that the modal average daily consumption as calculated from the volumes of composite proportional samples was about 2 litres,. This value corresponds with data from other sources. For some households an average daily

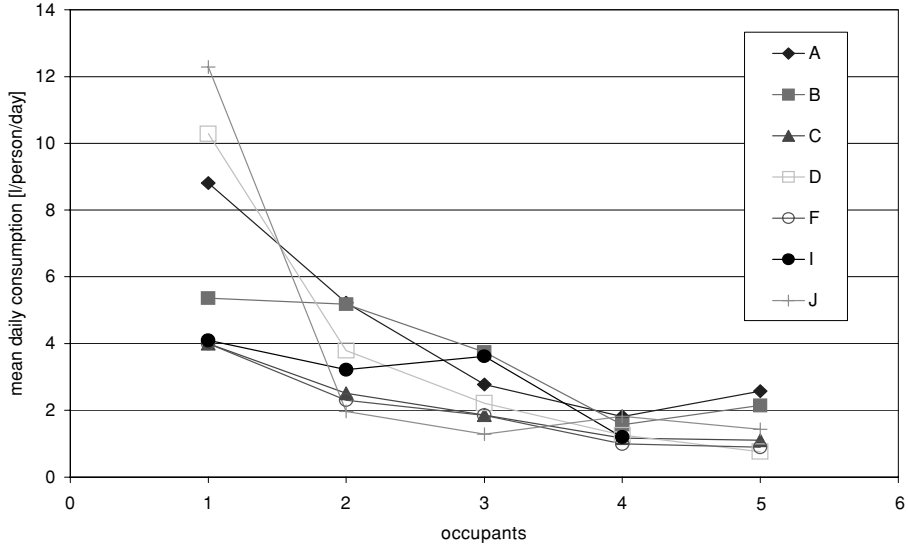


Figure 3.8 Mean daily consumption for different household sizes

consumption of about 10 litres was found. This might be explained by the fact that the occupants were at home during the whole test period. If the occupants had visitors during the test period, this would obviously increase the calculated average daily consumption.

Figure 3.8 shows that the average daily consumption depends on household size. This implies that the average weekly intake of lead by a consumer depends on the number of occupants sharing the same tap.

Both the modal daily consumption per occupant and the dependency on the household size are in accordance with data from other studies. This indicates that, in general, the composite proportional sampling device was operated correctly in the field test. There is some doubt over the apparently high consumption in one-person properties. These high values might stem from real high water use (e.g. tea, visitors, elderly people staying at home all day), but also from improper use of the device. Nevertheless no data have been excluded from the assessment on the basis of this criterion.

3.3.6 Representativeness of the Tested Protocols

The representativeness is judged both on supply area level and for individual properties. Representativeness of the protocols (PROT) is assessed on the basis of the following parameters:

- the relationship between PROT and COMP: both the slope (or x-coefficient) and the correlation coefficient (R^2) of the linear relationship;
- the ratio between PROT and COMP in individual properties;
- the 90 % prediction range of PROT around the parametric value;
- the ability to detect problem properties;
- the average value of tested protocols compared to the average COMP value in a supply zone.

Relationships between results sampling methods

Random daytime sampling (RDT) Figure 3.9 shows the results of the random daytime samples in all properties, compared to the composite proportional sample. Figure 3.9 indicates that the relationship between RDT and COMP showed considerable variation. In general, RDT seems to overestimate COMP (slope > 1), though for some individual properties RDT underestimates COMP. As a result of the variations the correlation coefficient, R^2, is 0.61.

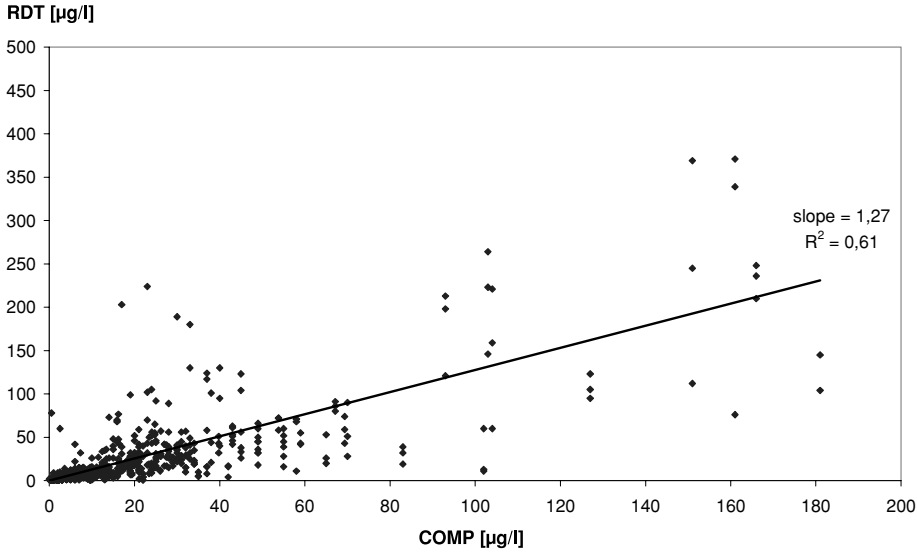


Figure 3.9 Results of RDT sampling in relation to COMP

Fully flushed (FF) Figure 3.10 shows the FF results, in relation to COMP. As can be seen, the relationship between FF and COMP showed considerable variation. FF generally underestimates COMP. In some cases, however, FF is considerably higher than COMP. This might indicate particle release due to flushing. As a result, R^2 is low: 0.29.

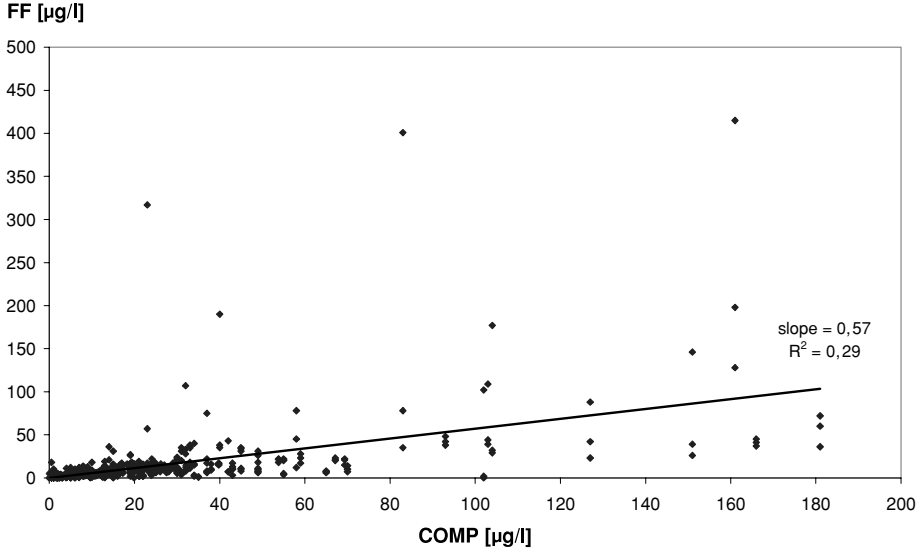


Figure 3.10 Results of FF sampling in relation to COMP

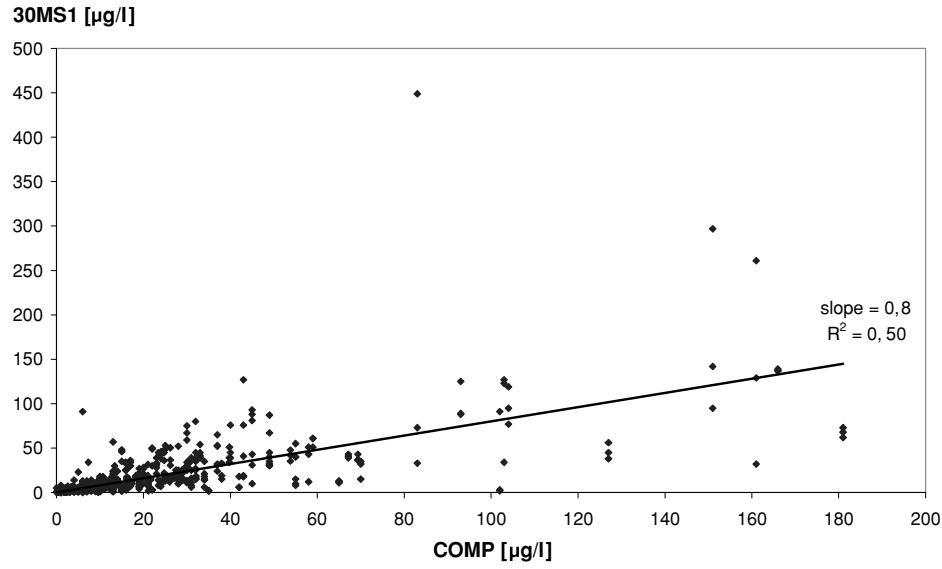


Figure 3.11 Results for 30MS1 samples in relation to COMP

30-Minute stagnation sample: first litre (30MS1) Figure 3.11 shows the results for the 30MS1 sampling procedure. The figure indicates that the relationship between 30MS1 and COMP varied. Generally, 30MS1 somewhat underestimated COMP. The variations resulted in a correlation coefficient, R^2 of 0.5.

30-Minute stagnation sample: second litre (30MS2) Figure 3.12 shows the results of the 30MS2 sampling, versus COMP. This figure indicates that the relationship between 30MS2 and COMP is comparable to the relationship between 30MS1 and COMP: both have a slope of 0.80. The correlation coefficient of 30MS2, however, is somewhat better, 0.56 instead of 0.50 (30MS1).

30-Minute stagnation sample: average of first and second litre (30MSA) Figure 3.13 shows the results of 30MSA sampling, in relation to COMP. The relationship between 30MSA and COMP was about the same as the relationship between the individual samples (30MS1 and 30MS2) and COMP, albeit that R^2 was improved somewhat by averaging 30MS1 and 30MS2. This is a result of averaging-out of extreme values.

Average of random daytime and fully flushed sample (av(RDT,FF)) Figure 3.14 shows the results of av(RDT,FF), in relation to COMP. As shown in the figure, averaging RDT and FF (av(RDT,FF)) resulted, in general, in an underestimation of COMP (slope = 0.92). The correlation of the FF samples to COMP (R2FF = 0.29) influences the correlation coefficient of av(RDT,FF). Consequently, R^2 of av(RDT, FF) is 0.63, which is somewhat less than R^2 of RDT (0.61).

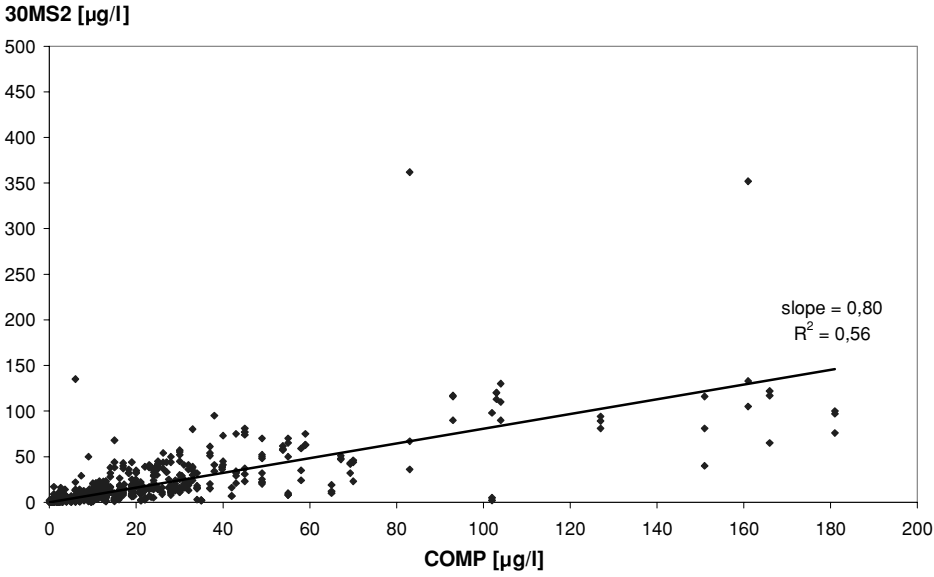


Figure 3.12 Results of 30MS2 sampling in relation to COMP

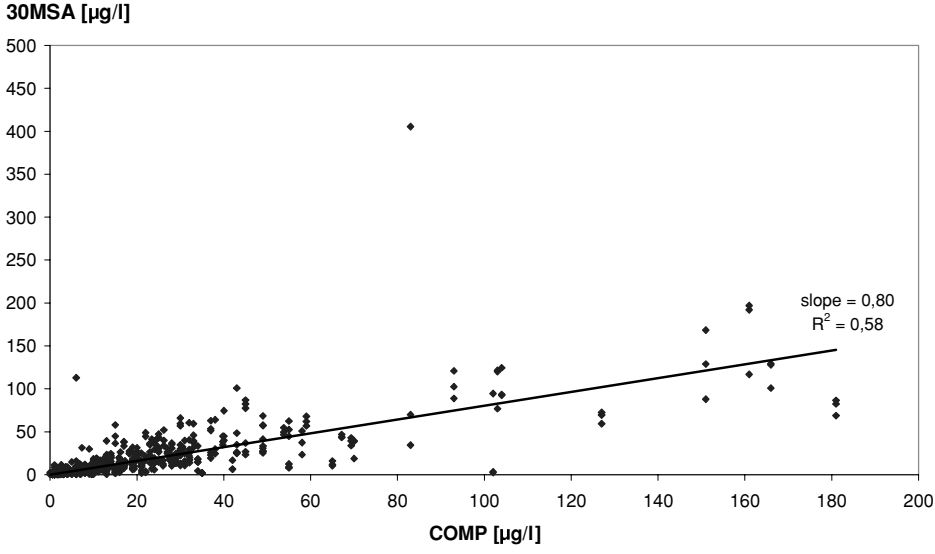


Figure 3.13 Results of 30MSA sampling in relation to COMP

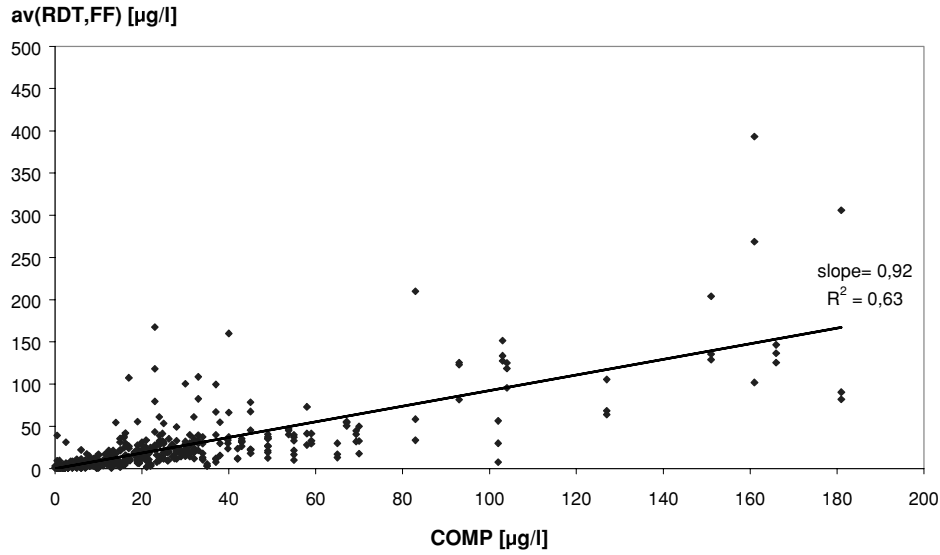


Figure 3.14 Results of av(RDT,FF) in relation to COMP

In summary, all tested sampling procedures show a linear relationship with the composite proportional sample, albeit that the correlation is poor. RDT and the 30-minute stagnation samples, 30MS1, 30MS2 and 30MSA show the best correlation ($R^2 \cong 0.5$–0.6). RDT however, generally seems to overestimate COMP (slope > 1), whereas 30MS somewhat underestimates COMP (slope > 1). FF clearly shows the poorest relationship to COMP: $R^2 = 0.29$ and the slope is 0.57.

Ratio between the tested protocols and the composite proportional sample

The ratio between the result obtained by the tested protocol and the result of the composite proportional sample is another way to express the representativeness of the sampling method. Before showing the results, the approach used is explained:

Ratio between PROT and COMP Ideally, the ratio between the lead values obtained by the tested protocol (PROT) and the composite proportional sample (COMP) should be unity, or at least constant over a wide concentration range. To determine the variation in the ratio between PROT and COMP, the average ratio is calculated over both the combined test areas (total, all results) and the individual test areas (A–K). The 95 % prediction range of the average ratio is:

$$\text{average} \pm 1.96 \frac{\sigma}{\sqrt{n}}$$

where $\sigma =$ standard deviation of ratio and $n =$ number of samples.

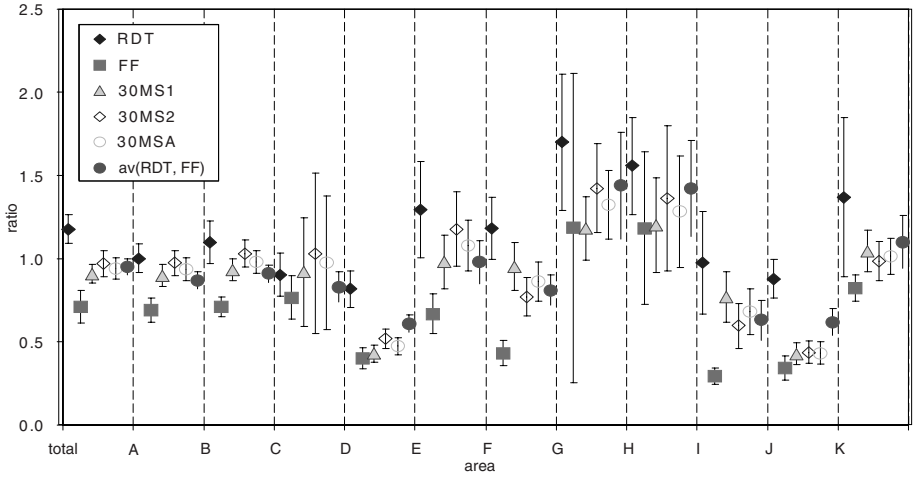


Figure 3.15 95 % prediction range of average ratio between PROT and COMP, for 0<COMP< 200 μg/l

A narrow prediction range indicates that the ratio is fairly constant over the concentration range involved.

Example: The average ratio between RDT and COMP samples of 60 samples taken in an area is 1.24, with a standard deviation of 1.05. With a 95 % probability the true average ratio is in the range of 1.24 ± 0.26.

The 95-% prediction range of the average ratio between the tested protocols and COMP was calculated for all test areas in the ranges 0–200 μg/l, 0–50 μg/l (the former parametric value), 0–25 μg/l (the interim PV) and 0–10 μg/l. The prediction ranges were calculated on the basis of individual samples (i.e. not averaging the three results from each property).

Figure 3.15 shows the 95 % prediction ranges of the average ratios, in the average weekly intake range of 0–200 μg/l (as determined by COMP). It shows that the average ratios between the tested protocols varied between test areas. Furthermore, the width of the prediction range (shown as bars in the figure) varied between areas. Generally however, the width of the prediction range hardly varied between the tested protocols (total, all areas).

The average ratio for RDT was generally higher than 1, whilst the ratio between FF and COMP was generally less than 1. In areas G and H, the average ratio of FF was greater than 1, and the prediction range was relatively wide. This may indicate release of particles during flushing.

The 30MS samples show comparable ratios and prediction ranges, generally somewhat less than 1. In areas D, I and J the average ratio was considerably less than 1 (0.5–0.7).

Figure 3.16 shows the 95 % prediction ranges of the average ratios, in the COMP range of 0–50 μg/l. Generally, the results were comparable to the results for the

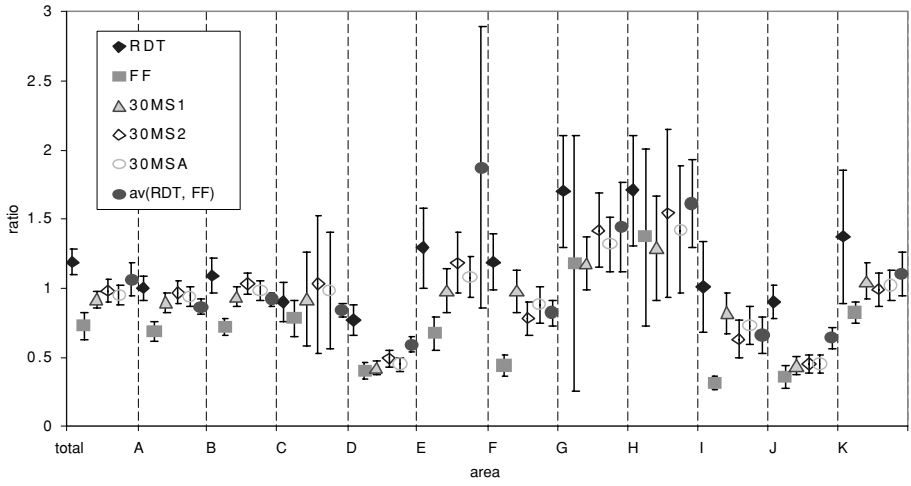


Figure 3.16 95 % prediction range of ratios between PROT and COMP, for 0<COMP<50 µg/l

COMP range of 0–200 µg/l. As the range of 0–50 µg/l included fewer samples, the 95-% prediction ranges for the average ratio were somewhat wider.

Figure 3.17 shows the 95-% prediction ranges of the average ratios, in the COMP range of 0–25 µg/l. As can be seen, the average ratios in the COMP range between 0 and 25 µg/l are comparable to the ratios found in the full range (0–200 µg/l).

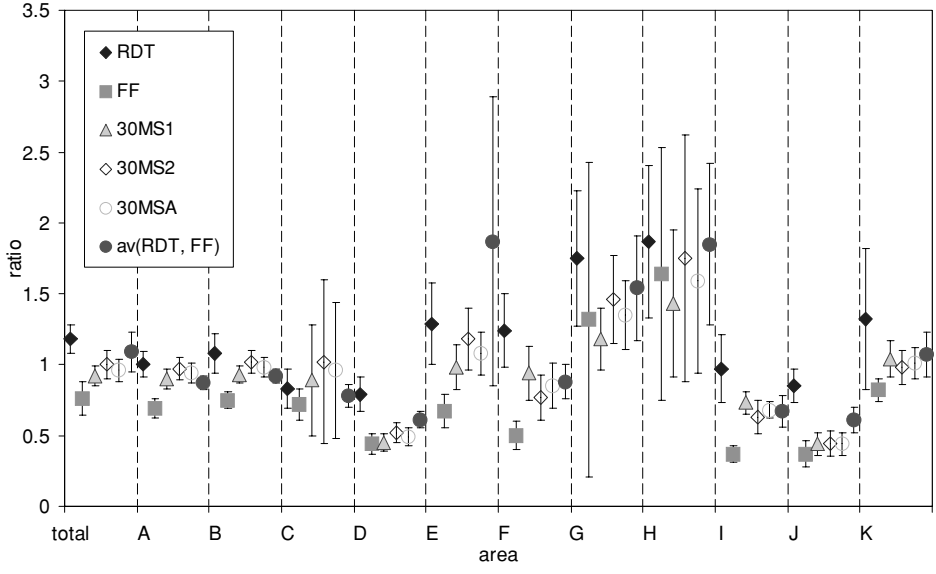


Figure 3.17 95 % prediction range of ratios between PROT and COMP, for 0<COMP<25 µg/l

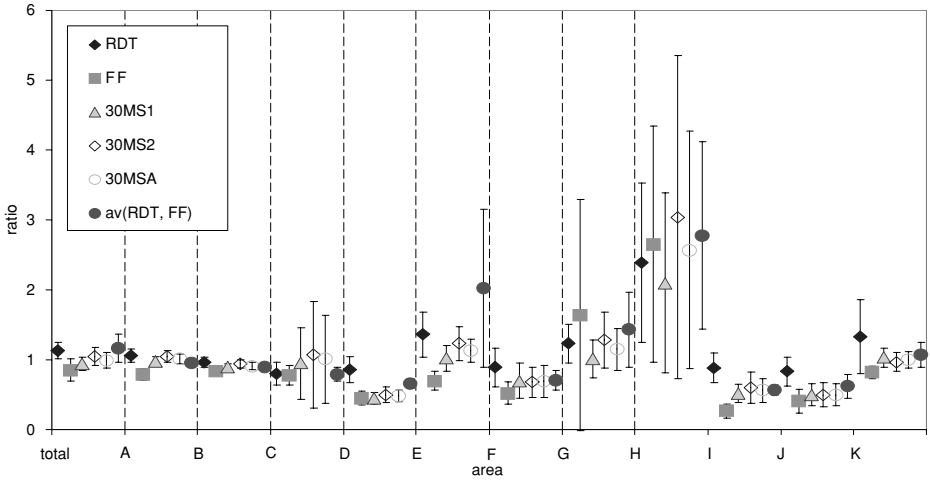


Figure 3.18 95 % prediction range of ratios between PROT and COMP, for 0<COMP<10 μg/l

Finally, Figure 3.18 shows the 95-% prediction ranges of the average ratios, for the COMP range of 0–10 μg/l. The figure indicates that in general, the average ratio between the tested protocols and COMP in the range of 0–10 μg/l is comparable to the average ratio in the full range of concentrations. In some areas, however, the 95-% prediction range seems very wide. This is due to the fact that in these areas only a few properties were found with lead concentrations (in COMP) below 10 μg/l.

Summarizing, assessing the performance of the selected protocol by calculating the ratio between results from the protocols and results from the composite proportional sample shows that RDT, 30MS1, 30MS2 and 30MSA performed best, i.e. the ratios were close to 1 and the 95-% prediction ranges were narrow in most test areas. FF generally underestimates COMP (ratio $\ll 1$). The average of RDT and FF does not give additional information.

The 90-% prediction range of the tested protocols The prediction range of a protocol reflects the accuracy of that protocol in predicting the value of the composite proportional sample. Therefore, the 90-% prediction range is applied to assess the representativeness of the tested protocols.

The method applied to determine the 90 % prediction range, can be explained as follows:

The trueness and precision for the prediction of COMP by the tested protocol can be expressed by the 90-% prediction range. In this way the average ratio between the tested protocol and COMP is taken into account, along with the variability or reproducibility of the protocol. The reproducibility is expressed as the relative range.

The 90-% prediction range is calculated as follows:

$$\text{90-\% prediction range} =$$
$$(\text{PROT/average ratio} \pm \tfrac{1}{2}\,\text{90 percentile of relative range} * \text{PROT})$$

where average ratio = average ratio between PROT and COMP, and 90 percentile of relative range = 90th percentile of relative range.

Example: The average ratio between RDT and COMP is 1.1, and the 90th-percentile of the relative range is 1.6 for 5 < COMP < 15 µg/l. If RDT is 10 µg/l, the 90 % prediction range for COMP is 9 ± 8 µg/l.

The 90 % prediction ranges have been calculated for concentrations of the tested protocols around 10, 25 and 50 µg/l. They were calculated on the basis of single samples taken at a property.

Figures 3.19 to 3.21 show the 90 % prediction range of the tested protocols around 10 µg/l, 25 µg/l and 50 µg/l, respectively. These figures include data from all test areas. As shown in Figure 3.19, the 90 % prediction ranges vary between protocols. For example if RDT is 10 µg/l, the range of predicted COMP will be 9 ± 8 µg/l, with a 90 % probability. The FF and 30MS samples show comparable prediction ranges. The 30MSA sample shows the best prediction range: 10 ± 4 µg/l.

At around 25 µg/l, the 90 % prediction ranges became much wider. If RDT is 25 µg/l, the range of predicted COMP was 22 ± 23 µg/l. The 90 % prediction range of FF at this concentration was 33 ± 14 µg/l. This range was narrower than for RDT,

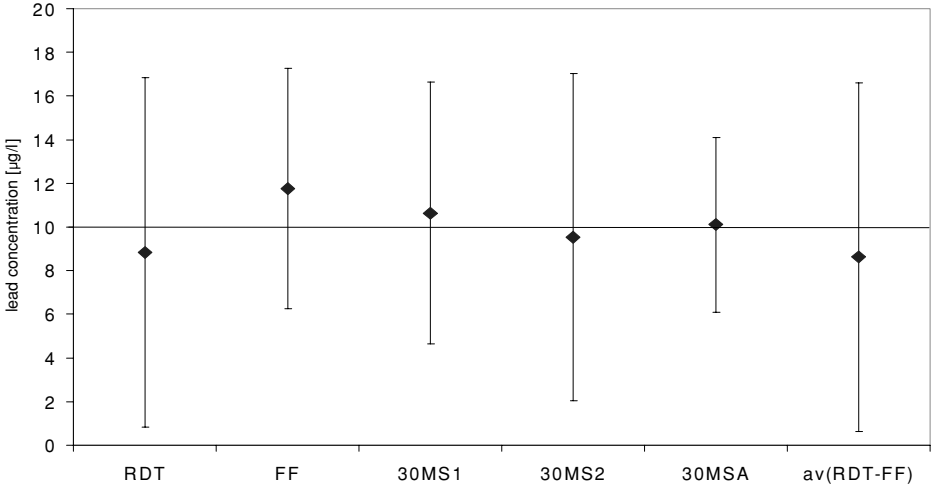


Figure 3.19 90 % prediction range around the parametric value of 10 µg/l

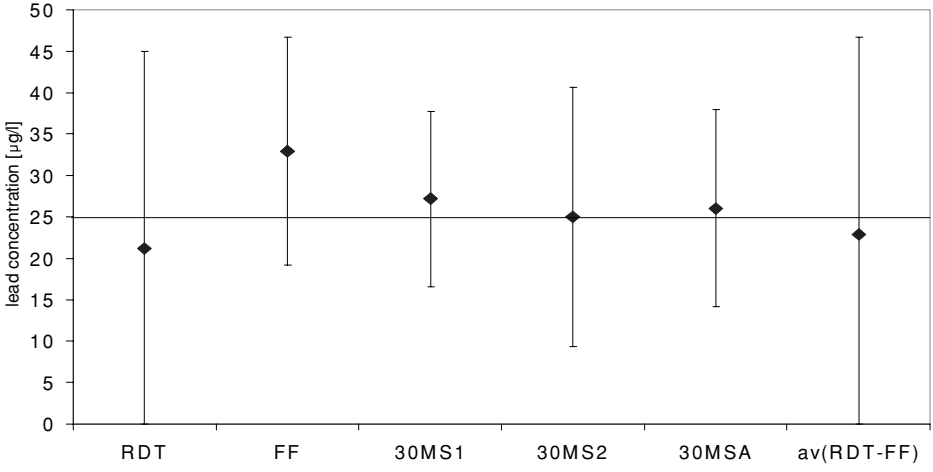


Figure 3.20 90 % prediction range around the interim parametric value of 25 µg/l

on average FF however tends to underestimate COMP. The 30MS samples show the best prediction: between 26 ± 10 µg/l (30MSA) and 25 ± 15 µg/l (30MS2).

As Figure 3.21 indicates, all tested protocols showed wide prediction ranges around 50 µg/l. For example if FF was 50 µg/l, the 90 % prediction range of COMP was 73 ± 74 µg/l. Again 30MSA gave the most narrow prediction interval: 52 ± 27 µg/l.

Summarizing, 30MSA gives the most accurate reflection of the weekly average concentration, as determined by composite proportional sampling.

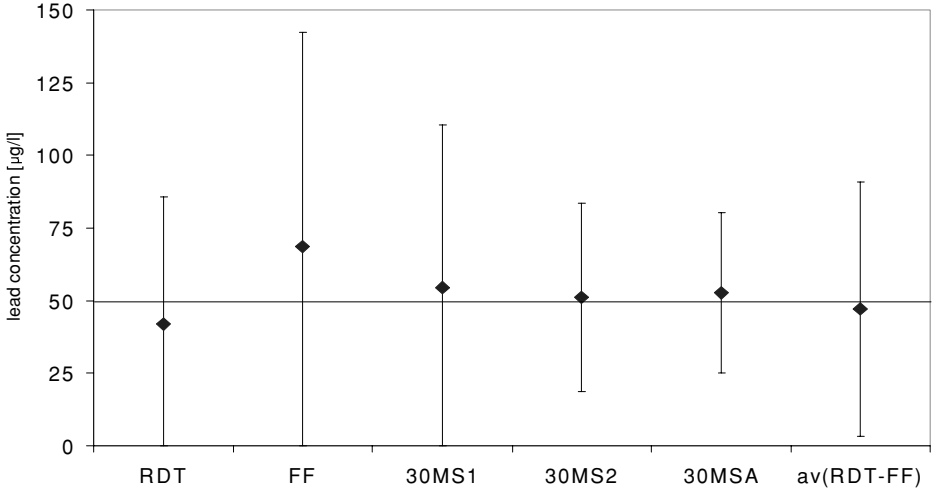


Figure 3.21 90 % prediction range around the former parametric value of 50 µg/l.

3.3.7 Reproducibility of the Tested Protocols

Reproducibility

The reproducibility of the test procedures is expressed as the coefficient of variation, or relative range, of the three samples of one type taken in one property:

$$\text{Relative range} = (\max - \min)/\text{mean}$$

Ideally, the relative range is 0 (max = min). The value of the relative range may differ between properties and test areas. Therefore the frequency distribution of relative ranges has to be calculated. The cumulative relative frequency of the relative ranges of the protocols shows the difference in reproducibility of the protocols. The relative range, furthermore, may depend on the lead concentration.

Example: The 90th-percentile of the relative range of PROT is 0.4 in the range of COMP between 5 and 10 µg/l. If the result of PROT is 10 µg/l, we can assume with 90 % probability that PROT is between 8 and 12 µg/l.

Figure 3.22 shows the relative cumulative frequency distribution of the relative range of results of three samples in one property, for all procedures. As shown, the RDT samples exhibit the widest relative range of results. This can be explained by the fact that the stagnation time is not controlled for the RDT sample, whereas stagnation time is controlled for both the FF and 30MS samples. Still, the relative ranges of all procedures seem relatively wide. If, however, we consider the wide ranges of results for composite proportional samples, the reproducibility of FF and

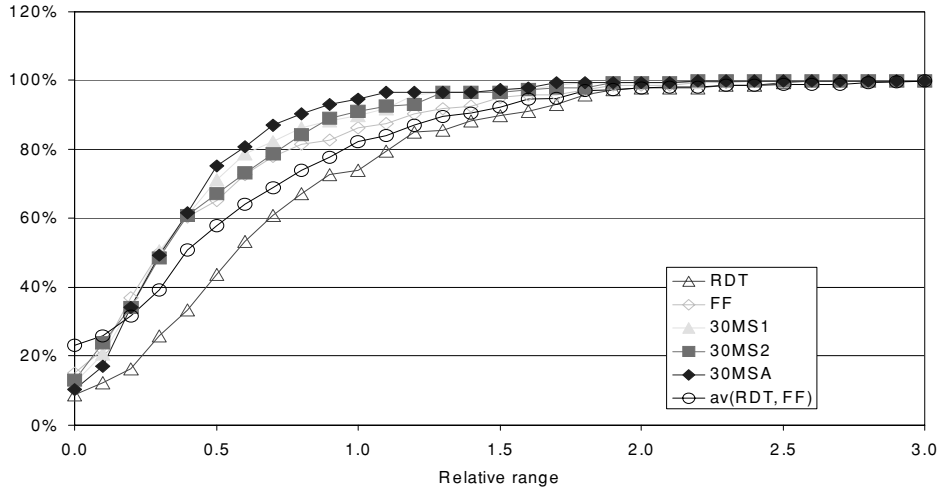


Figure 3.22 Relative range of results of three samples in one property

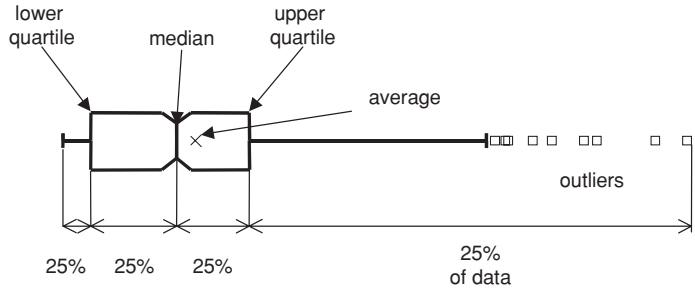


Figure 3.23 Box and whisker plot

30MS is comparable to the reproducibility of the reference procedure (COMP). This can be explained by the fact that FF and 30MS results are not influenced by consumer behaviour.

Box and Whisker plots

Frequency distributions can also be presented in so called 'box and whisker' plots (Figure 3.23). These plots show the relevant characteristics of the frequency distribution: lower quartile, median, upper quartile and outliers.

Example: If the median is 0.4, for 50 % of all samples the relative range is less than 0.4.

Figure 3.24 shows the box and whisker plot of the relative ranges for lead concentrations (as determined by COMP) in the full data range 0–200 µg/l.

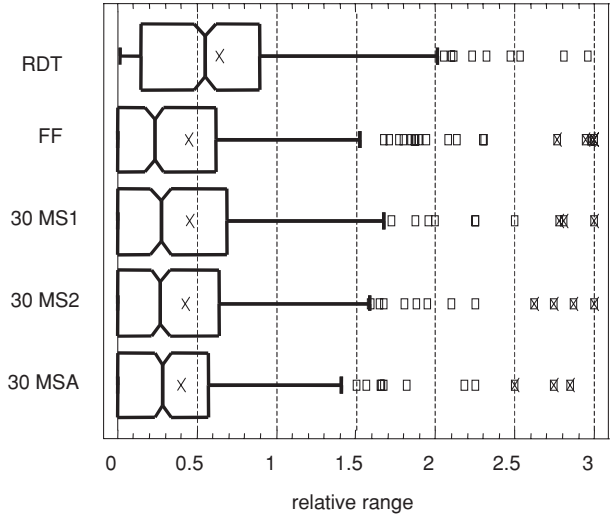


Figure 3.24 Box and whisker plot of the relative range for the full data range (289 properties)

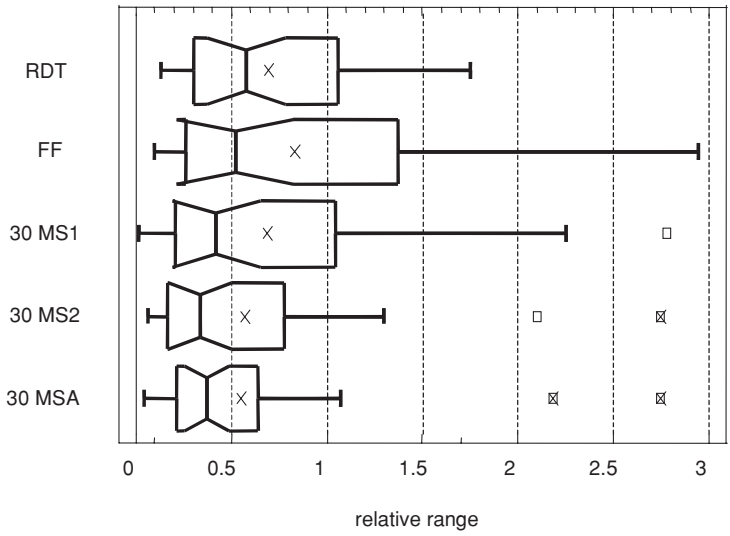


Figure 3.25 Box and whisker plot of the relative range for lead concentrations between 35 and 200 $\mu g/l$ (32 properties)

As shown in this figure, in all properties RDT shows variation (relative range >0). This is due to the fact that the stagnation time of these samples is variable and not known. In at least 25 % of properties, FF and 30MS samples do not vary across the three sampling days. In this range (0–200 μg/l) the reproducibility of 30MS and FF samples is comparable.

Figure 3.25 shows the box and whisker plot for the concentration range of 35 to 200 μg/l. The range includes 32 properties. The figure shows that the relative ranges of all protocols at high concentration (between 35 and 200 μg/l) are higher than the relative ranges for the full concentration range, i.e. the variability increases with concentration. The outliers of the relative range in the concentration range between 0 and 200 μg/l are accounted for in the relative ranges found in properties with lead concentrations above 35 μg/l.

Figure 3.26 shows the box and whisker plot for the concentration range of 15 to 35 μg/l, around the interim PV of 25 μg/l. This range includes 64 properties. As shown in the figure, the relative ranges of all protocols are less for properties with lead concentrations in the range of 15 to 35 μg/l, than in properties with high lead concentrations. The relative ranges, and therefore the reproducibility, for the FF and 30MS samples are better than for RDT.

Finally, Figure 3.27 shows the box and whisker plot for the concentration range of 5 to 15 μg/l, around the PV of 10 μg/l. This range includes 68 properties. As the figure indicates, in this concentration range the relative ranges of FF and 30MS samples are comparable, albeit that 30MSA samples (the average of 30MS1 and 30MS2) seem to perform somewhat better in terms of reproducibility. Still, the median value

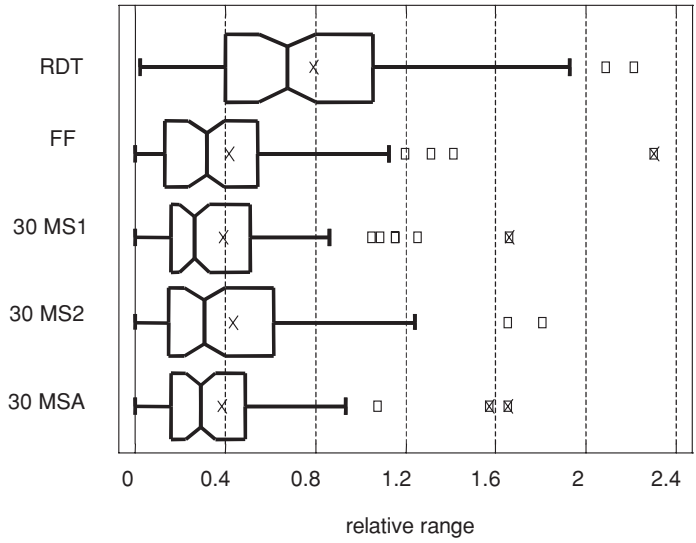


Figure 3.26 Box and whisker plot of the relative range for lead concentrations between 15 and 35 $\mu g/l$ (64 properties)

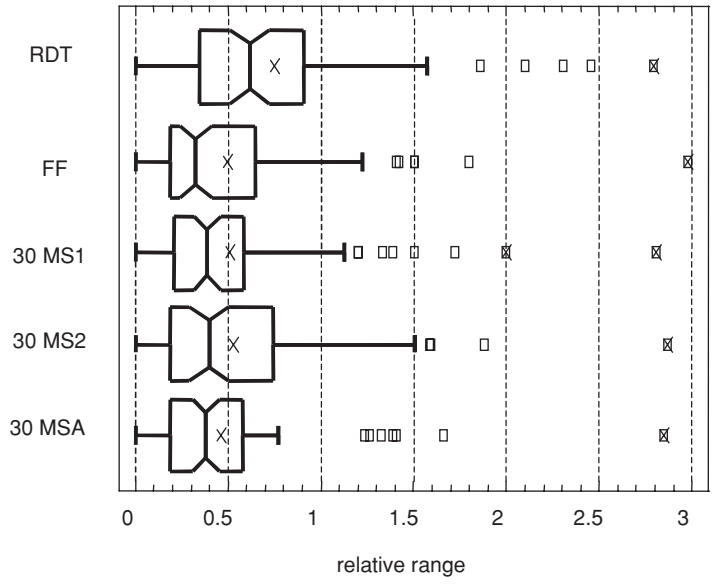


Figure 3.27 Box and whisker plot of the relative range for lead concentrations between 5 and 15 $\mu g/l$ (68 properties)

for the relative range of these procedures is about 0.4. This means that for 50 % of the tested properties, the results of three samples vary between 8 and 12 μg/l, if the average value is 10 μg/l. In this concentration range, the median relative range of RDT is about 0.6. Consequently, in 50 % of the tested properties the RDT samples vary between 7 and 13 μg/l, at an average RDT of 10 μg/l.

3.3.8 Costs, Practicality and Consumer Acceptance

Costs

Because of the different tariffs in different countries, it is not possible to compare directly the costs of the different protocols. Therefore, Table 3.4 gives a comparison of time needed for taking the samples according to the different procedures, not taking into account travelling time to the consumer. The write-off of the composite proportional sampling device is about 15 Euro per property sampled. The time range is chosen to take into account the probability that a procedure fails (e.g. the composite proportional sample overflows) and the sample has to be taken again. The time for COMP includes consumer information. The times are based on experience from the field tests.

Example of monitoring costs: Under the following assumptions, we can calculate costs for the different monitoring protocols:

- cost for manpower (sampler, including the use of a car): 75 Euro/hour;
- average travel time between properties: 15 minutes;
- analysis costs (including consumables): 30 Euro/sample;
- write-off of sampling device: 15 Euro/property.

Table 3.4 Time required for sampling for different procedures

Procedure	Time needed by sampler	Practicality	Consumer acceptance
COMP	60–75 min[a]	Poor	Poor
RDT	5–10 min	Good	Good
FF	10–15 min	Good	Good
30MS[b]	45–60 min	Moderate	Moderate

[a] At least two visits to one property: one to install the sampling device, one to collect the sample and sampling device.
[b] Two samples need to be analysed.

Using the times given in Table 3.4, this results in the following costs:

- COMP: 158–176 Euro
- RDT: 55–61 Euro
- FF: 61–68 Euro
- 30 MS: 105–124 Euro

This example shows that the differences in monitoring costs are considerable. The composite flow proportional sample, as expected, is the most expensive. For the costs of one COMP sample, three properties can be sampled using RDT! Obviously the 30-minute stagnation time makes 30MS protocols expensive.

Practicality

Practicality covers several aspects of the procedure, such as is the procedure easily applicable, are skilled samplers needed, does the procedure need specific tools, etc. A practical method is easily applied (score: good), an impractical method needs more attention (score: poor).

Consumer acceptance

Consumer acceptance is a very important factor. It might take a lot of time to find enough properties where consumers would be willing to cooperate, if the sampling procedure bothers consumers too much. This is obvious in the case of the composite proportional sample, but consumers might also object to a sampler waiting for 30 minutes in their property to take a stagnation sample.

Table 3.4 summarizes the evaluation of costs (time), practicality and consumer acceptance.

3.3.9 Final Evaluation of Sampling Procedures

According to the Drinking Water Directive, lead monitoring at the tap should be based on ‘representative sampling’ at the consumer’s tap. The lead value determined by a monitoring protocol should be very close to the true average weekly intake. This approach ensures the safety of individual consumers. The sampling method should be ‘representative’ and accurate.

Five sampling procedures are evaluated on the basis of representativeness (i.e. the accuracy in determining the weekly average intake and the ability to detect problem

properties), reproducibility and cost effectiveness, practicality and consumer acceptance.

Random daytime sampling (RDT) is defined as a sample taken at the consumers' tap at a random, unannounced, time during office hours. At a composite COMP lead level of 10 μg/l, the 90 % prediction range of RDT is 9 ± 8 μg/l. Nevertheless, in the European study, RDT enables detection of 83 % of properties where the lead concentration of the proportional sample exceeds 10 μg/l (problem properties under the Drinking Water Directive). The number of falsely detected properties amounts to 10 %. The reproducibility of RDT sampling is poor (the median relative range is 0.6 at lead levels around 10 μg/l). In terms of costs, practicality and consumer acceptance, RDT is the most favourable protocol.

Fully flushed sampling (FF) is defined as a sample taken at the consumers' tap after flushing the plumbing system for at least three pipe volumes. The 90 % prediction range of FF at a COMP level of 10 μg/l is 12 ± 6 μg/l. Furthermore FF enables detection of only 45 % of problem properties, whereas it results in 4 % false positives. FF is very cost effective, practical and acceptable to consumers.

30-Minute stagnation time sampling (30MS) is defined as a sample taken at the consumer's tap after flushing the plumbing system for at least three pipe volumes and allowing the water to stand for 30 minutes. In this study, three types of 30MS sample have been evaluated: the first litre sample (30MS1), the second litre sample (30MS2) and the average of 30MS1 and 30MS2, 30MSA. These procedures perform comparably, although 30MSA shows somewhat better representativeness and reproducibility. The accuracy of 30MSA is the best of the tested protocols. At a COMP lead concentration of 10 μg/l, the range of 30MSA is 10 ± 4 μg/l. The 30MS samples are capable of detecting 76 % of problem properties, whereas the amount of false positives is 6 %. In terms of cost effectiveness, practicality and consumer acceptance, 30MS scores lowest of the tested protocols, because of the time involved.

The unexpectedly good performance of RDT sampling can be explained by the fact that, in general, it seems to overestimate the average weekly intake, as determined by COMP. Apparently, RDT sampling as defined in this study (samples taken unannounced, during office hours, by a professional sampler) relates to a stagnation time close to or higher than the actual average inter-use stagnation time. The RDT sample contains history of water use at the tap shortly before the sample was taken. Stated otherwise, unlike FF and 30MS, RDT, to some extent accounts for the water consumption pattern of the consumer. In terms of reproducibility 30MS and FF sampling perform best. This can be explained by the fact that both protocols reflect water composition and household installation, but not the variable behaviour of the consumer, which does influence the RDT result. Despite the differences in performance as to representativeness for individual properties, all procedures show the same trend in lead levels found at a distribution area level.

3.3.10 Experience with the Monitoring Protocol in France

Following the outcome of the European project for developing a new protocol for the monitoring of lead in drinking water, field experiments were carried out in France to test and develop practical tools for assessing compliance/noncompliance for lead (Baron, 2001). Experiments were carried out in five supply areas in France, each supply area being a geographical unit supplied by a uniform water quality. In each area a random selection of at least 60 addresses was made. In each property three samples were taken at the kitchen cold water taps using the protocols as described in the European study on lead monitoring and as described before (EUR19087, 1999):

- RDT sample;
- fully flushed sample;
- 30 MS.

No composite proportional sample was taken.

The results from the measurements broadly confirmed the conclusions of the European study. At zone level, RDT or 30MS samples taken in a sufficient number of properties gave almost identical results. RDT is slightly more severe but, above all, it is more practical and acceptable to the consumer.

At individual level (one consumer tap), the French study showed that RDT was not sufficiently reproducible for the assessment of the average concentration based on a single sample. The 30-MS (2l) protocol is more reproducible and representative and is to be preferred in this situation, because with the 30-MS protocol the sampling conditions can be fully controlled by the sampler.

Just as in the European study, FF sampling seemed not to be representative of the average concentration, and only gave an indication of the minimum lead concentration at the tap.

3.4 FIT FOR PURPOSE LEAD MONITORING PROTOCOLS

3.4.1 The Requirements for Sampling and Monitoring Lead in Accordance with the DWD 98/83/EC

Annex I of Council Directive 98/83/EC on the quality of water intended for human consumption has in part B – chemical parameters – entries for the parameters lead (PV of 10 μg/l), copper (PV of 2 mg/l) and nickel (PV of 20 μg/l). There is a note (Note 3) added to the parameters lead, copper and nickel and also a note (Note 4) to the lead parameter. These notes read as follows:

Note 3:

The values apply to a sample of water intended for human consumption obtained by an adequate sampling method at the tap and taken so as to be representative of a weekly average value ingested by consumers. Where appropriate the sampling and monitoring methods must be applied in a harmonised fashion to be drawn up in accordance with Article 7(4). Member States must take account of the occurrence of peak levels that may cause adverse effects on human health.

Note 4:

For water referred to in Article 6(1)(a), (b) and (d), the value must be met at the latest, 15 calendar years after the entry into force of this Directive. The parametric values for lead from five years after the entry into force of this Directive until 15 years after its entry into force is 25 μg/l.

Article 6 specifies the point of compliance:

1. The parametric values set in accordance with Article 5 shall be complied with: (a) In the case of water supplied from a distribution network, at the point, within premises or an establishment, at which it emerges from the taps that are normally used for human consumption.
2. In the case of water covered by paragraph 1(a), Member States shall be deemed to have fulfilled their obligations under this Article and under Article 4 and 8(2) where it can be established that non-compliance with the parametric values set in accordance with Article 5 is due to the domestic distribution system or the maintenance thereof except in premises and establishments where water is supplied to the public, such as schools, hospitals and restaurants.
3. Where paragraph 2 applies and there is a risk that water covered by paragraph 1(a) would not comply with the parametric values established in accordance with Article 5, Member States shall nevertheless ensure that:
   (a) appropriate measures are taken to reduce or eliminate the risk of noncompliance with the parametric values, such as advising property owners of any possible remedial action they could take, and/or other measures, such as appropriate treatment techniques, are taken to change the nature or properties of the water before it is supplied so as to reduce or eliminate the risk of the water not complying with the parametric values after supply; and
   (b) the consumers concerned are duly informed and advised of any possible additional remedial action that they should take.

3.4.2 Sampling and Monitoring Strategy

To give more information on the sampling of the metals according to the DWD 98/83/EC, a decision from the commission is under discussion with the member states. The current proposal, which is outlined hereunder, may be modified further to the ongoing negotiations.

Audit monitoring

General requirements The purpose of audit monitoring is to provide the information necessary to determine whether or not all of the directive's parametric values are being complied with. All parameters set in accordance with Article 5(2) and (3) must be subject to audit monitoring unless it can be established by the competent authorities, for a period of time to be determined by them, that a parameter is not likely to be present in a given supply in concentrations that could risk of a breach of the relevant parametric value.

Monitoring of lead, copper and nickel

Harmonized method: The method to be used for monitoring in supply zones is the method of random sampling during the day (see Note 1, below). Monitoring must be carried out at the supply tap and at frequencies provided for the audit monitoring.

Alternative method: The member states may use the fixed stagnation time sampling method (see Note 2, below), which takes better account of the local or national situation, provided that in the supply zones, it does not lead to fewer breaches of the parametric values than would be the case using the harmonised method.

Where the alternative method is used, the member states will supply the commission with the appropriate information regarding its implementation (including the stagnation time used) and the justification.

Additional monitoring: In order to increase consumer health protection and improve knowledge about exposure to lead, copper and nickel through drinking water, the member states are urged to increase monitoring and sampling in accordance with the Community guidelines on the monitoring of lead, copper and nickel (see Note 3, below).

Notes:

(1) Random monitoring during the day is defined as taking a sample of water directly from the tap that is usually used for consumption (without taking a sample from, flushing or cleaning the tap before the sample is taken) at a randomly chosen time during the day (during 'normal' working hours).

(2) Monitoring using the fixed stagnation time is defined as emptying and refilling the installation, taking no water from the system for a fixed amount of time and then sampling directly from the tap that is usually used for consumption.

(3) Community guidelines for the monitoring of lead, copper and nickel in accordance with the requirements of Council Directive 98/83/EC on the quality of water intended for human consumption.

3.4.3 Lead Monitoring Purposes

General applications

Monitoring of lead may serve the following applications:

- statutory monitoring in order to check compliance with the Council Directive and national regulations;
- zone assessment;
- assessing/predicting the effect of measures taken to reduce lead in drinking water, such as adjustment of water composition at the treatment facility;
- consumer information on the actual lead intake via drinking water. In case of exceedance of the PV, the monitoring protocol should be able to indicate who is responsible for taking action.

Statutory monitoring The Drinking Water Directive has the following requirement with respect to representativeness of the monitoring of lead in drinking water:

> The value applies to a sample of water intended for human consumption obtained by an adequate sampling method at the tap and taken so as to be representative of a weekly average value ingested by consumers. Where appropriate the sampling and monitoring methods must be applied in a harmonized fashion to be drawn up in accordance with Article 7(4). Member States must take account of the occurrence of peak levels that may cause adverse effects on human health' (Note 3, part B, Annex I).

On the basis of this study either RDT sampling, as defined in this study, or 30MS are appropriate protocols for statutory monitoring purposes.

Zone assessment A sufficient number of samples needs to be taken in order to provide statistically valid information on the lead concentrations within a supply zone. The minimum sampling frequencies given in the directive are insufficient in the case of lead. Typically, at least 20 properties should be sampled, whichever sampling

method is used. For small supply systems fewer samples may be appropriate, depending on local circumstances.

RDT or 30MS sampling are appropriate for identifying areas that require priority action to reduce lead levels. Previous studies show that the lead pipe test (pipe rigs at the treatment facility) can also be suitable for this purpose.

Assessing/predicting the effect of measures A distinction should be made between measures taken at the treatment facility and measures taken at specific properties. To evaluate the effect of measures taken at the treatment facility (pH increase, orthophosphate dosing, etc.), both the RDT sampling procedure and the lead pipe test are appropriate. For prediction purposes the lead pipe test is most convenient.

Measures for individual houses consist of lead pipe replacement and flushing before drawing water for consumption. The effect of the first measure can be established using 30-minute stagnation-time sampling and proportional sampling. To assess the effectiveness of flushing, the fully flushed protocol can be applied.

Consumer information To give the consumer an accurate, and repeatable, value for the average weekly lead concentration, the best approach is 30MS sampling. If, however, the objective is simply to assess compliance or noncompliance, either RDT or 30MS samples can be used. For specific purposes the composite proportional sampling method can be utilized. Identifying causes of observed exceedance of the PV for lead, and thus of responsibility for taking action, should be achieved by 30-minute-stagnation-time samples. After the stagnation period, a number of consecutive 1-litre samples should be taken, corresponding to the dimensions of the service pipes and the house installation.

Special applications

A property where the average weekly lead concentration exceeds the parametric value is considered to be a 'problem property'. The ability of a protocol to detect such properties can be assessed as follows.

The ability to detect problem properties The *ability of a protocol to detect problem properties* can be expressed as the percentage of 'positives' during the tests. A test is considered positive if both the protocol (PROT) and the reference (COMP) give a value above the parametric value (PV). The *percentage of positives* is the number of properties where both PROT and COMP exceed the PV, divided by the number of properties where COMP exceeds the PV, or:

$$\text{positives}\,[\%] = (\text{COMP and PROT} > \text{PV})/(\text{COMP} > \text{PV})^{*}100\,\%$$

The protocol should give a realistic estimate of the problems in an area, in order to be used as an effective decision tool. Furthermore the results of the protocol should not

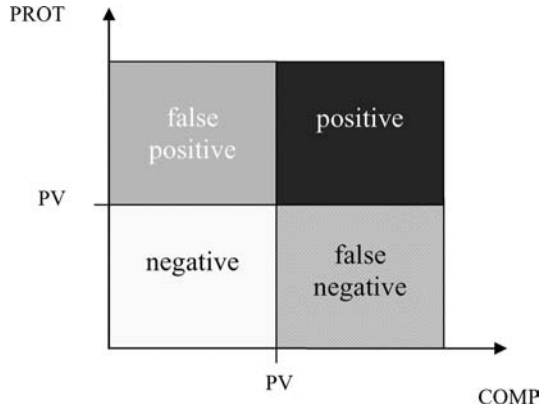


Figure 3.28 Definition of positives and false positives

unnecessarily worry consumers. In other words, the percentage of 'false positives', properties where PROT exceeds the PV, whilst COMP is less than the PV should be low. The *percentage of false positives* is the number of false positives divided by the total number of positives, or:

$$\text{false positives}\,[\%] = (\text{PROT} >, \text{COMP} < \text{PV})/(\text{PROT} > \text{PV})^{*}100\,\%$$

Figure 3.28 illustrates the definitions mentioned above.

The *false negative* in Figure 3.28 indicates the percentage of *not detected* problem properties. *Negative* indicates the percentage of properties where the lead concentration is *below* the parametric value. Ideally, the percentage of positives should be 100 % and the percentage of false positives should be close to 0 %.

Figure 3.29 shows the ability of the tested protocols to identify problem properties for the combined test area. All tested protocols are able, to a certain extent, to identify problem properties. The failure to identify a problem property or the false identification of a property as a problem property is likely to be caused by characteristics of the plumbing system.

About 80 % of the properties that are not detected by the protocols have lead service pipes and more than 5 metres of non-lead internal plumbing (copper, galvanized steel or plastic). Also the average weekly lead concentration in these properties is generally low to moderate (10–20 μg/l). In this type of property a large volume of water stands in the household installation. Depending on the design of the installation, the number of users who share the household installation and the service pipe, a volume of water that has stood in the lead service pipe for a longer period reaches the consumers' tap at a given moment. Random daytime sampling has at least a chance of detecting this effect. Fully flushed and 30-minute stagnation-time samples tend to overlook this effect because they are based on a completely flushed system.

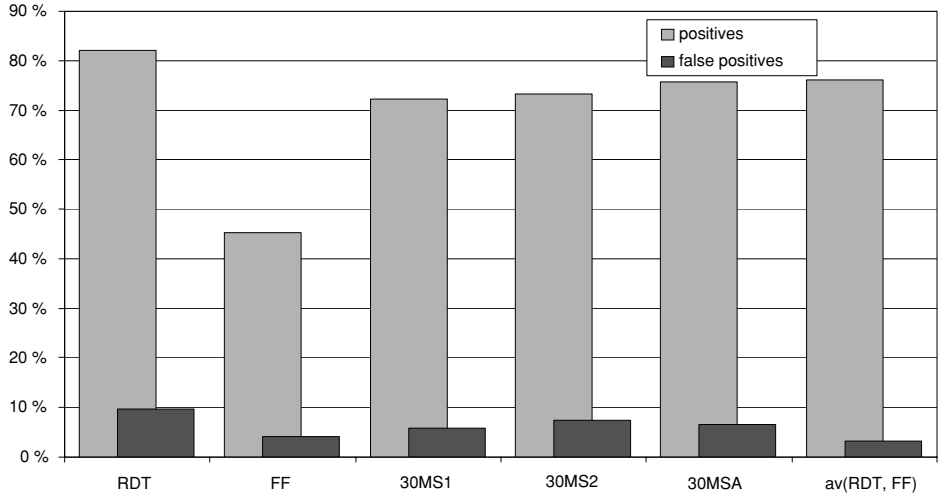


Figure 3.29 Identification of problem properties at a parametric value of 10 $\mu g/l$

In this case 30MS sampling would only be able to detect lead concentrations above 10 µg/l by taking a very large sample volume.

Figure 3.30 shows the lead concentration distribution in undetected problem properties for the tested protocols.

On the other hand, properties falsely identified as problem properties have plumbing systems similar to undetected problem properties. Again 80 % of these properties have lead service pipes, and about 20 % have lead plumbing. These properties are

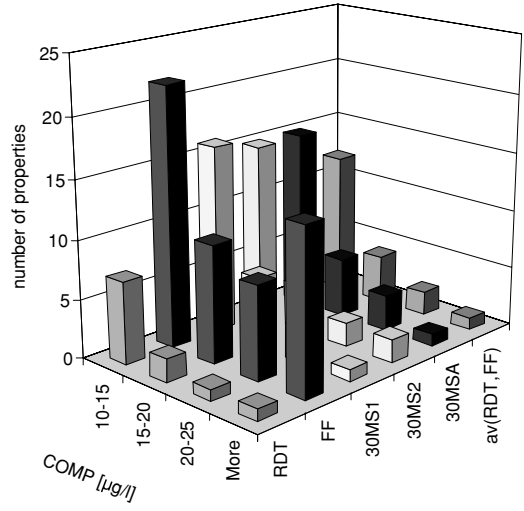


Figure 3.30 Lead concentration distribution in undetected problem properties

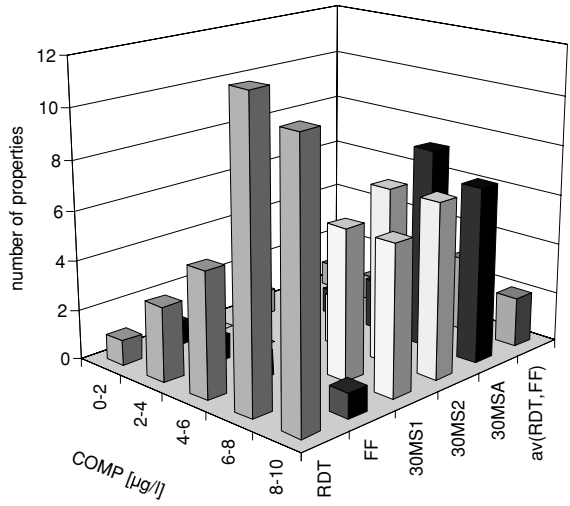


Figure 3.31 Lead concentration distribution in falsely identified problem properties

potential problem properties, and here the consumer behaviour is the dominating factor in determining whether COMP is less than 10 µg/l or not. The lead concentrations of the COMP samples in these properties are generally between 6 and 10 µg/l.

Figure 3.31 shows the lead concentration distribution for properties falsely identified as problem properties.

Approaches for improving detection of problem properties Taking more samples at the same tap (on different visits) can increase the ability of protocols to detect problem properties. This will also unavoidably increase the number of false positives. Therefore, an optimal compromise should be reached between assuring the safety of an individual consumer and the safety of a group of consumers (distribution area).

During the field test three samples of each sample type were taken in each property. Based on three test results we can define two approaches:

- one of three samples exceeds the PV: *positive* if COMP also exceeds the PV, *false positive* if COMP is less than the PV;

- the mean of three samples exceeds the PV: *positive* if COMP also exceeds the PV, *false positive* if COMP is less than the PV.

Figures 3.32 and 3.33 show the results of these approaches for the total test area.

These figures show that the percentage of positives is hardly improved by taking three samples at one property, but that the percentage of false positives rises somewhat. Taking three samples in one property increases the sampling costs drastically.

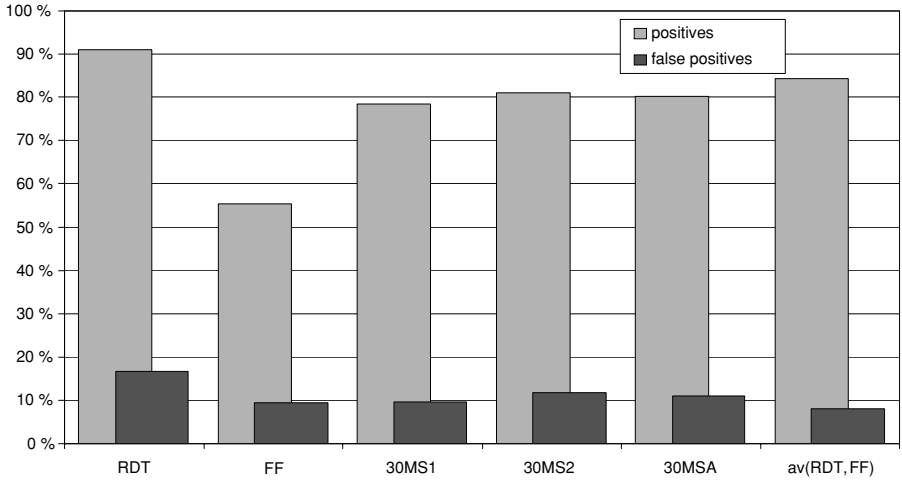


Figure 3.32 Properties detected where at least one of three samples exceeds 10 $\mu g/l$

Setting priorities for the intermediate PV Five years after implementation of the DWD, a transitional period of 10 years starts when the PV for lead in drinking water is set at 25 μg/l. Water companies will take appropriate control measures to lower plumbosolvency. To set priorities, distribution areas will have to be tested. From the results of the field test we can calculate the following:

- the probability that a protocol recognizes a property where lead exceeds 25 μg/l: positive if PROT > 25 μg/l when COMP > 25 μg/l, false positive when PROT > 25 μg/l and COMP < 25 μg/l;

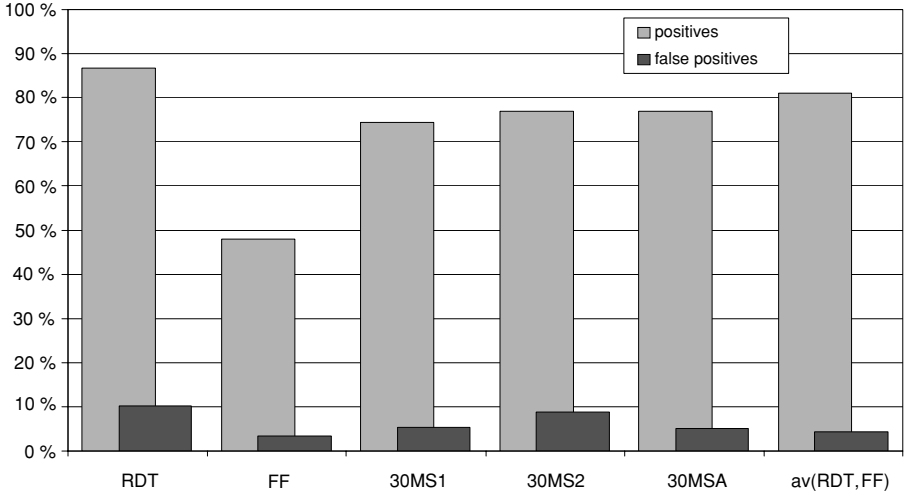


Figure 3.33 Properties detected where the average of three samples exceeds 10 $\mu g/l$

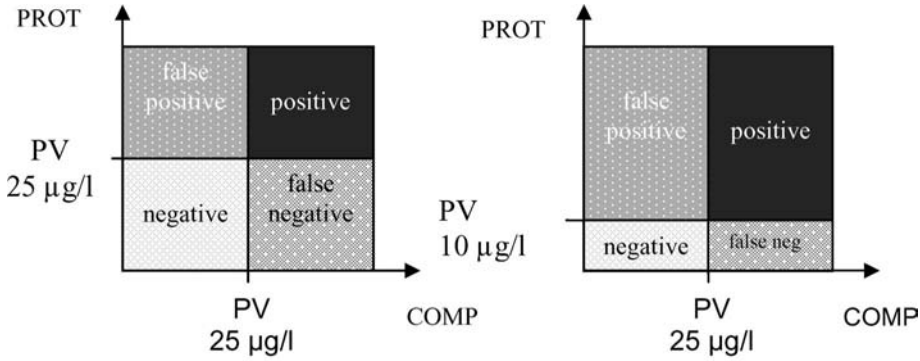


Figure 3.34 Priorities for intermediate PV

- the probability that a protocol recognizes a property where lead in COMP exceeds 25 µg/l, when the PV for PROT is set at 10 µg/l (Figure 3.34).

The results for both approaches, applied to the properties sampled during the field test, are given in Figures 3.35 and 3.36.

These graphs show that for both approaches RDT is more capable of detecting properties with lead exceeding 25 µg/l. The COMP values for the false positives are generally in the range of 10 to 25 µg/l, so lead levels in these properties are in the concentration range where measures will have to be taken in the future (to comply with the PV of 10 µg/l).

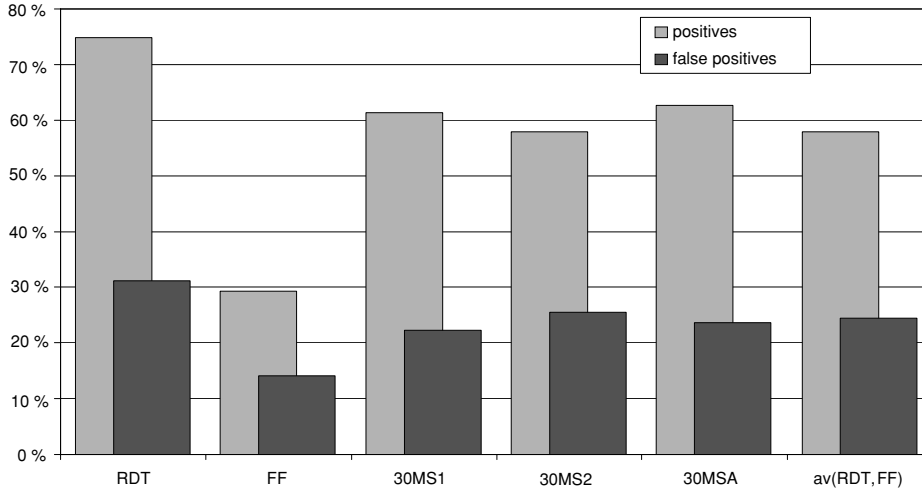


Figure 3.35 Detection of properties with lead > 25µg/l at a PV of 25 µg/l

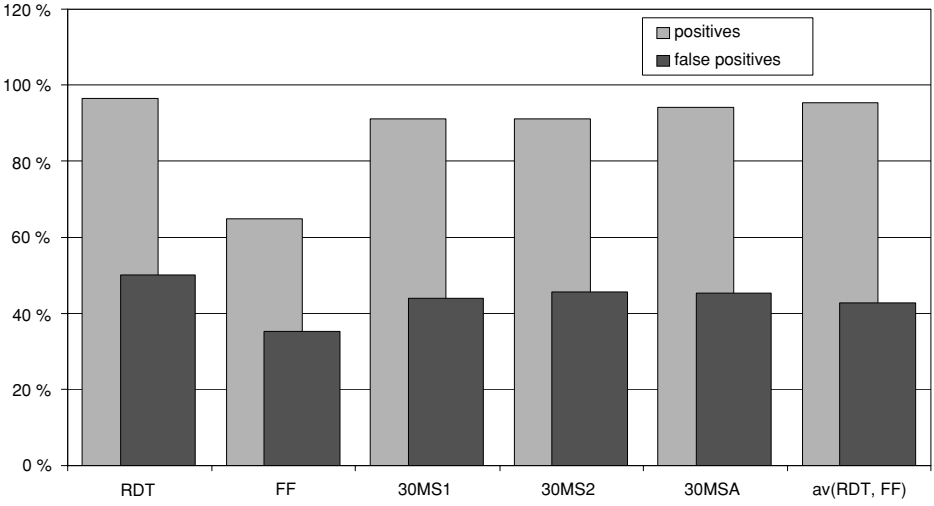


Figure 3.36 Detection of properties where lead $> 25 \mu g/l$ at a PV for protocols of 10 $\mu g/l$

Setting priorities for water treatment

When considering measures to decrease the lead content, water companies need to have a representative value for the average lead intake in a supply zone. Figure 3.37 shows the averages of the results for all protocols in all test areas. As shown, RDT and 30MS generally give the best estimate for the average concentration in a test

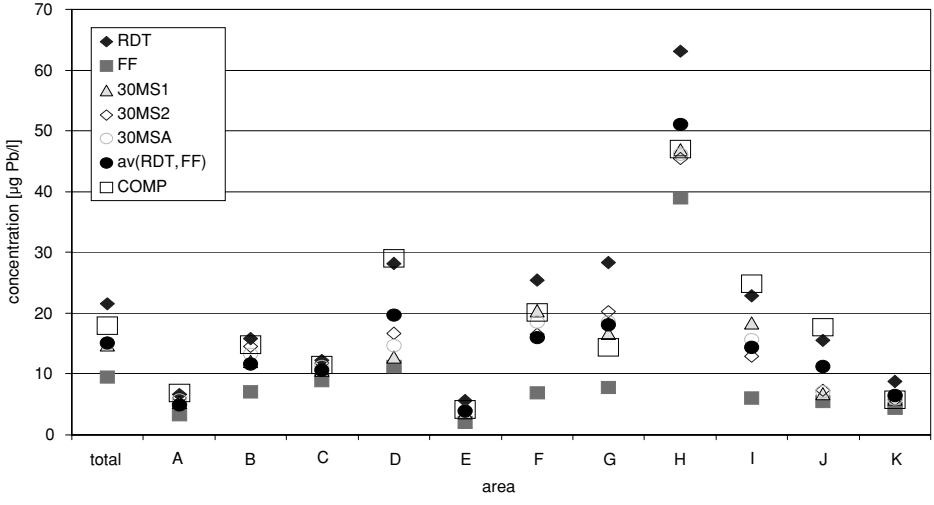


Figure 3.37 Averages of all protocols for all test areas

area. FF however, underestimates the average. In areas D, I and J, only RDT gave a good estimation of the average lead concentration (as determined by COMP). In areas F, G and H the average of RDT substantially exceeded the average of COMP.

3.5 LEAD LEVELS IN DRINKING WATER IN TAP WATER

3.5.1 Overview Lead Levels in Test Areas

The sampling programme as given in Figure 3.6 was carried out in about 230 properties in areas with a water quality as defined in Table 3.3. The lead levels in the test areas measured with the composite proportional sample technique varied from less than the detection limit to about 200 μg/l. The results are summarized in Figure 3.38, which shows the lead concentration distribution for the test areas, and in Table 3.5, which gives the values of composite proportional sampling in all test areas. In about 60 % of the tested lead plumbed properties, the lead concentrations were higher than 10 μg/l. For installations without lead pipes, in 5 % of the properties the lead concentrations were higher than 10 μg/l.

Even though test areas and properties were selected where the lead was expected to be significant (69 % of the tested properties had lead service pipes and/or lead plumbing), only 44 % of the composite proportional samples exceeded the PV of 10 μg/l. About 20 % of all composite proportional samples exceeded the intermediate PV of 25 μg/l and 19 % exceeded the value of 50 μg/l.

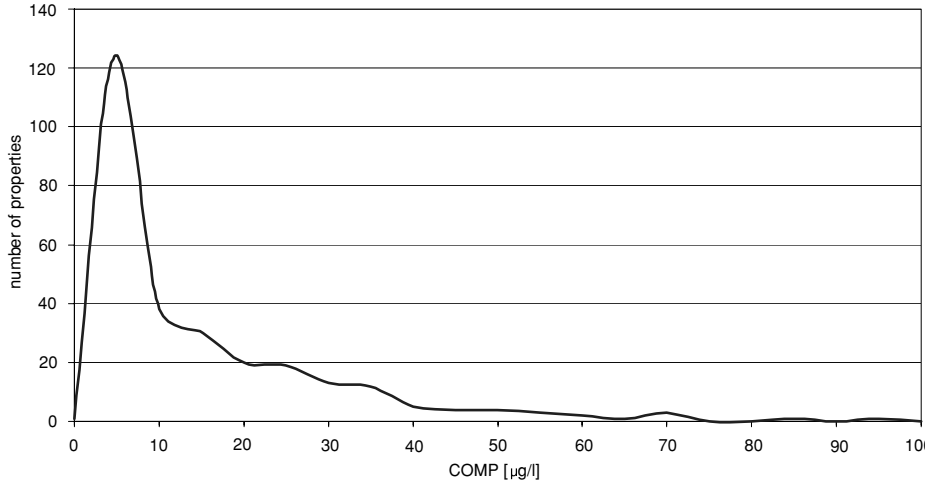


Figure 3.38 Lead concentration distribution throughout combined test area as determined by composite proportional sampling (EUR 19087,1999)

Table 3.5 Values of COMP in test areas

		Lead concentrations in COMP [μg/l]					
Area	Data	Min.	Max.	Median (50 %)	Upper quartile (75 %)	Lower quartile (25 %)	90 % percentile
Total	289	0	181	7.0	21.0	2.5	38.4
A	27	2	21.6	3.3	8.9	2.0	18.8
B	27	2	53.8	4.7	14.3	2.0	23.1
C	31	1	55	7.0	13.8	2.0	31.2
D	30	1	181	15.5	28.5	8.5	73.4
E	29	0.5	20	3.0	5.0	1.0	9.6
F	29	1	69	16.0	30.5	2.3	45.8
G	25	0.5	45	5.8	20.0	1.9	27.6
H	30	0	166	28.5	58.8	14.3	107.8
I	13	3	55	26.0	34.0	12.0	46.6
J	16	3	65	13.0	22.8	7.0	31.5
K	34	1	33	2.5	5	2.5	12.4

The range of lead concentrations, based on composite proportional sampling, in this study varied from below the detection limit to 181 μg/l. Of the 294 investigated properties, 44 % showed lead levels above 10 μg/l (new PV), and 20 % above 25 μg/l (intermediate PV). Given the relatively high percentage of lead plumbed houses (69 %) in the tested population of properties, these percentages are relatively low. The lead concentrations found in properties without lead pipes vary from below detection limit to 23 μg/l. In only 7 % of these properties does the composite proportional sample exceed 10 μg/l. A high proportion of properties in supply areas with high pH waters and/or orthophosphate dosing showed lead levels below 25 μg/l.

Flushing the tap before use is an effective measure to reduce considerably the lead concentration at the consumer's tap. However, flushing does not guarantee that the lead level will be below 10 μg/l. This study shows that in 50 % of properties where the composite proportional sample exceeded 10 μg/l, the fully flushed sample was less than 10 μg/l. For 70 % of properties where lead exceeded 25 μg/l, the lead concentration after flushing was less than 25 μg/l.

3.5.2 Effect of Water Composition

The effect of water composition cannot be determined clearly from the results in this test, as there is a large variation in plumbing systems and household situations within and between test areas. In the areas where orthophosphate is dosed (A, J and K, partly), the lead levels were significantly lower, but samples from some properties still exceeded the parametric value of 10 μg/l.

The representativeness of the protocols can, at least partly, be explained by the variation in lead concentration ranges between test areas, for example:

- area E : 75 % of data < 5 μg/l, 90 % < 10 μg/l. This explains the poor representativeness;
- area D, F, H, I and J : high concentrations;
- area H and I : very few low concentrations (<10 μg/l);
- area B, C (and G) : same variation ranges and comparable results in representativeness.

3.5.3 Effect of Plumbing Materials

To assess the effect of plumbing materials on the lead concentration as determined by composite proportional sampling, we distinguish the following situations:

- all properties, regardless of installation materials;
- properties with lead service pipes and/or lead plumbing;
- properties with no lead pipes;
- properties without lead, with galvanized steel pipes;
- properties without lead, with copper pipes.

The assessment is carried out on the assumption that the details of the plumbing system were noted correctly by the sampler. In some areas however, it proved extremely difficult to check service pipe and plumbing materials, especially in cases where pipes were hidden behind wall plaster. Figure 3.39 shows the lead concentration frequency for the situations mentioned above.

This figure shows that for installations without lead pipes, the parametric value of 10 μg/l was exceeded in 7 % of these properties. Generally, the intermediate parametric value of 25 μg/l was met in properties without lead pipes. In about 40 % of the tested lead-plumbed properties, the lead concentration complied with the parametric value of 10 μg/l.

3.5.4 Water Consumption

The European study has generated data on daily water consumption throughout Europe. It appears that there are no significant differences in domestic water consumption per person between the tested countries. On average, water consumption amounts to about 2 litres per person per day. The daily water consumption per

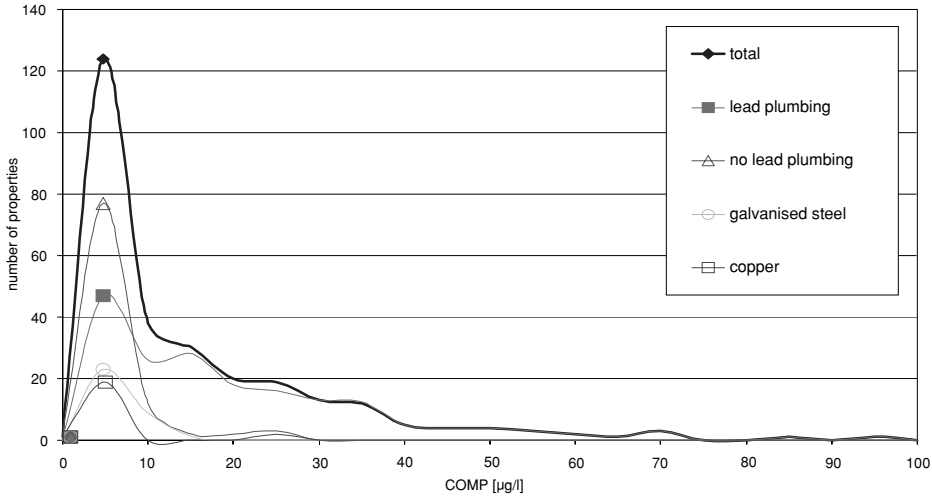


Figure 3.39 Lead concentration frequency for different plumbing systems

occupant decreases with increasing number of occupants from 5–10 litres a day in a one-person household, to 1.5 litres a day in a five-person's household. The high consumption in a one- or two-person household can be explained by the fact that not all water drawn for dietetic purposes is actually consumed, and that these households (in our study) consist mainly of elderly people, who might stay at home all day.

REFERENCES

Baggelaar, P. K. and C. G. E. M. van Beek (1995), Suggestions for the optimisation of large scale ground water quality assessment, *Kiwa report KOA* 95.107 (in Dutch), Nieuwegein, The Netherlands

Bailey, R. J. and P. F. Russel (1981), Predicting drinking water lead levels. *Environmental Technology Letters* **2**, 57–66.

Bailey, R. J., D. Holmes, P. K. Jolly and R. F. Lacey (1986a), Lead concentrations and stagnation time in water drawn through lead domestic pipes, *WRc Report TR 243*.

Bailey, R. J., P. K. Jolly and R. F. Lacey (1986b), Domestic water use patterns, *WRc Report TR 225*.

Baron, J. (2001), Monitoring strategy for lead in drinking water at consumer's tap: field experiments in France, *Water Science Technology: Water Supply* **1**, 193–200.

Britton, A. and W. N. Richards (1981), Factors influencing plumbosolvency in Scotland, *Journal of the Institution of Water Engineers and Scientists* **35**(5), 349–364.

CEC (1980), Council Directive relating to the quality of water intended for human consumption, *Official Journal of the European Communities*, No. L229, 23, 30th August 1980, 11–29 (80/778/EEC).

EUR19087 (1999), Developing a new protocol for the monitoring of lead in drinking water, *Final Report European Commission DGXII*. Project team: Th. J. J. van den Hoven, P. J. Buijs, P. J. Jackson, P. Leroy, J. Baron, A. Boireau, J. Cordonnier, M. H. Marecos do Monte, M. J. Benoliel, I. Wagner.

Gregory, R. (1990), Galvanic corrosion of lead solder in copper pipework, *Journal Institution of Water and Environmental Management*, **4**(2), 112–118.

Haring, B. J. A. (1984), Lead in drinking water, Thesis, University of Amsterdam, The Netherlands.

Kuch, A. and I. Wagner (1983), A mass transfer model to describe lead concentrations in drinking water, *Water Research* **17**(10), 1303–1307.

Leroy, P. (1993), Lead in drinking water – origins, solubility, treatment, *Journal Water SRT – Aqua*, **42**(4), 233–238.

Packham, R. F. (1971), The leaching of toxic stabilisers from unplasticised PVC water pipe: Parts I-III, Water treatment and examination **20**, 108–164.

Poels, C. L. M. and G. Dibbets (1982), The initial migration by lead of unplasticised PVC water pipes, *H2O*, **15** (21), 588–590 (in Dutch).

Randon, G. (1996), Summary of the collective work carrried out by AGHTM concerning the presence of lead in tap water, *AGHTM Congress*, London, May 1996.

Schock, M. R. (1989), Understanding control strategies for lead, *Journal of the American Water Works Association* **81**(7), 88–100.

Schock, M. R. (1990), Causes of temporal variability of lead in domestic plumbing systems, *Environmental Monitoring and Assessment* **15**, 59–82.

Schock, M. R. (1994), Response of lead solubility to dissolved carbonate in drinking water, *Journal of the American Water Works Association* **72**(12), 122–127.

Sheiham I. and P. J. Jackson (1981), The scientific basis for control of lead in drinking water by water treatment, *Journal of the Institution of Water Engineers and Scientists*, **35**(6), 491–515.

Tielemans, M. W. M., J. W. F. Spiering and H. Brink (1995), Pellet softening at the Scheveningen treatment plant (DZH): Significant reduction of the lead and copper content of drinking water, *H2O*, **28** No. 21; 646 (in Dutch).

Vewin (1987), Advice for the approach to the problem of lead in drinking water (in Dutch) VEWIN = the Association for Dutch Water Campanies. It can be located at: VEWIN, P.O. Box 1019, 2280 CA Rijswijk.

Van den Hoven, Th. J. J. (1986), Lead in drinking water, *KIWA-report 96*, Nieuwegein, The Netherlands (in Dutch).

Van den Hoven, Th. J. J. (1987), A new method to determine and control lead levels in tap water, *Aqua* **6**, 315–322.

Wagner, I. (1992), Internal corrosion in domestic drinking water installations, *Journal Water SRT -Aqua*, **41**(4), 219–223.

WHO (1993), *Guidelines for Drinking Water Quality*, second edition, Volume 1, *Recommendations*, World Health Organization, Geneva.

4

Materials in Contact with Drinking Water

Jean Baron*

* Chapters 4.2 and 4.3 are based on a co-normative research report (report EUR 19602 EN-2000) carried out by a European Consortium.

Analytical Methods for Drinking Water: Advances in Sampling and Analysis Edited by P. Quevauviller and K. C. Thompson © 2006 John Wiley & Sons, Ltd. ISBN: 0-470-09491-5

4.1 PARAMETERS USED FOR THE CONTROL OF MATERIALS EFFECTS

The materials used in the construction of drinking water treatment and distribution systems must not affect negatively the quality (organoleptic, toxicological) of the water that is supplied to the consumer.

In order to prevent such negative impact of materials on drinking water quality, it is necessary that all materials and products intended for contact with drinking water can be appropriately assessed and approved before being installed. The European Acceptance Scheme (EAS), which is being developed, will define harmonized rules and principles for such assessment. The range of assessments to be carried out can vary depending on product and material composition characteristics, in particular, it may be different for organic, cementitious or metallic materials.

The formulation of the materials is the first step in the assessment of a product, with reference to lists of accepted substances (positive lists, composition lists) based on toxicological evaluation.

Laboratory testing is usually the second step of the assessment to be carried out, to ensure that after contact with a product drinking water quality will not pose significant risk to health and will comply with the DWD for organoleptic, chemical and bacteriological parameters.

The range of assessment which are or may be necessary is developed in Sections 4.1.1 to 4.1.4 below.

4.1.1 Organoleptic Assessments

The DWD requires that odour, flavour, colour and turbidity of drinking water must be acceptable to the consumer and that no abnormal changes occur.

Odour and flavour

Abnormal odour and/or flavour are an indication of major degradation of water quality. Although bad odours and flavours can be generated by other sources, such as contamination of the drinking water source, experience has shown that materials can readily cause significant problems. Some materials have the capability of leaching into drinking water substances at very low concentrations (often undetectable analytically) that give rise to unacceptable odour and flavour. Testing to ensure that products do not lead to such contamination is a major part of the assessment.

Colour and turbidity

Colour and turbidity of water can also result from migration or interaction between water and materials. Abnormal changes in these parameters are not acceptable to the consumer.

4.1.2 General Hygiene Assessments

Total organic carbon (TOC)

TOC gives an indication of the overall leaching of organic substances from a material. While there is no direct relationship between the organic matter (TOC gives no indication of its composition), and any particular effect on water quality and risk for the consumer, it is necessary to minimize any contribution from materials on this parameter.

Chlorine demand

Interaction between materials and water, or migration of substances, can influence the consumption of chlorine. A chlorine demand test can then be carried out in order to ensure that a material is relatively inert.

4.1.3 Substances that Pose a Risk to Health

Drinking water directive parameters

Chemical parameters, as specified in the DWD, shall be assessed if their presence is indicated during the examination of the formulation of a material.

Positive list substances

Organic substances that have been identified in the formulation of a material have to be measured to ensure that migration limits are not exceeded.

Unsuspected organic substances

An assessment for unsuspected organic substances needs to be carried out in order to reveal the presence of any chemicals in a product that are not indicated by formulation information. Such substances are detected by a procedure based on gas chromatography and mass spectrometry (GCMS).

Composition list substances (metals)

The risk of migration of metallic substances used in the formulation of metallic materials (alloying elements or impurities) must be assessed with regard to their toxicity and also for possible impact on organoleptic quality of drinking water (odour, colour and turbidity).

Cytotoxicity assessment

Migration of substances in water can give rise to cytotoxic effects. A cytotoxicity test can provide an overall assessment of the impact of a material on water quality in addition to chemical analysis. Research has been carried out to develop a harmonized and reliable test procedure. Cytotoxicity testing is part of the assessment in some European countries but it is still unclear as to whether or not it will be part of the European Acceptance Scheme.

4.1.4 Enhancement of Microbial Growth

Tests to assess the potential of materials to enhance microbial growth are used in some European countries. At the European level, research has been carried out and additional research is still necessary to develop a harmonized procedure.

4.2 TEST PROCEDURE FOR METALLIC MATERIALS

4.2.1 Introduction

Background

Materials used for the distribution and treatment of drinking water are not allowed to release substances that affect the quality of the water negatively (toxicological, organoleptic).

The EC Drinking Water Directive is being used as the examination file, although this Directive does not cover all the parameters that are important in the judgement of materials. Hence, the different European countries have regulations and approval schemes for the admittance of products or materials that come into contact with drinking water. Within harmonizing the different approval schemes in Europe, it is the aim of CEN TC164 /WG3 to develop standards for test methods for all materials versus water quality to be used in the assessment of hygienic and toxicological properties.

Metals and alloys are the most common materials in use for domestic installations. To comply with European and national regulations on the quality of water intended for human consumption, it is necessary to take into consideration the interactions between these materials and water.

With the assessment of metallic materials, some problems occur because metallic materials are strongly influenced by water quality and operating conditions. Because water quality and operating conditions are very diverse over Europe, no general conclusions can be drawn about metal release by metallic materials.

From traditionally used materials, such as lead and copper pipes, some relationships are known between water quality and metal release. However, little information

is available on alloys and new materials coming onto the market. These new materials and alloys must not give problems in complying with regulations.

Scope of the research

The general objective of conormative research was to provide background information in order to produce test methods for metallic materials. Within this scope a short-term test was evaluated and compared with long-term ('rig') tests to determine whether metals can be tested and admitted on the basis of short-term tests.

4.2.2 Metallic Materials

Metallic materials in use in drinking water installations

In Europe only a few types of metallic material are being used in plumbing systems. The regulations in the different member states allowing these materials show some differences; also the percentages of the different materials in drinking water installations show some variations. Metallic materials used in plumbing systems are:

- copper;
- copper alloys, such as brass, gun metal and bronze, which contain up to about 7 % lead, and may also contain a number of additives or impurities (e.g. arsenic, antimony or nickel in gun metal);
- stainless steels, which are alloys of iron that contain at least 12 % chromium, and may contain nickel (Cr-Ni stainless steel) and other elements such as molybdenum;
- galvanized steel. The lining of galvanized steel pipes consists of zinc, which can contain up to 1 % lead. Steel itself contains much less lead (up to 0.01 %);
- lead. Although, in many European countries the use of lead pipes is banned or not recommended, lead pipes are still found in old houses;
- combinations of these materials.

Parameters influencing metal release

Collecting information on metal concentrations at the tap is very complex because the metal release by pipes is strongly influenced by the characteristics of the drinking water, the presence and properties of corrosion layers on metal surfaces, the design of the plumbing system and the flow rate and flow regime of the water through the pipe.

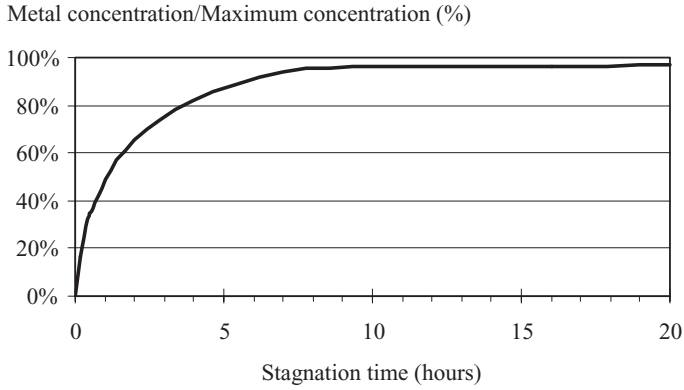


Figure 4.1 Typical stagnation curve of a metallic pipe material in contact with drinking water

Water characteristics For most of the common pure materials such as lead, iron, copper and zinc some relationships have been found between water composition and corrosion and metal migration behaviour (AWWA, 1996; Van den Hoven and van Eekeren, 1988; Wagner, 1992).

In general, in metal drinking water pipes the metal concentration increases rather quickly with time and remains for a time more or less at a constant level, depending on water quality (Van den Hoven and van Eekeren, 1988) (Figure 4.1). From these data it appears that the pH and hydrogen carbonate content in the water play a determining role in the corrosion of these materials. For example, in The Netherlands, rig tests have been performed on a large scale with copper pipes for different water qualities. Models developed on the basis of these results aim to predict copper concentrations at the tap after 24 hours of stagnation time. For instance, for copper pipes the following expression was found in The Netherlands:

$$Cu_{max}\ (mg/l) = 0.52\ TIC\ (mmol/l) - 1.37\ pH + 0.02\ [SO_4^{2-}]\ (mg/l) + 10.2$$

where TIC (Total Inorganic Carbon) stands for the total concentration of carbon dioxide, bicarbonate and carbonate.

This relationship is valid after initial ageing of the material when it is already 'stabilized'. It has been established with slow continuous flow of water.

From the expression for Cu_{max} it can be seen that the copper solubility is strongly dependent on the water quality. For other materials there will be different relationships with water quality. Therefore it is necessary to test the metal release by materials in water of different qualities.

However, very little information is available about the effect of water quality on alloys that are on the market. In the future, new materials can be expected with unknown composition and properties. Additional information is needed on the tendency of other trace metals, like arsenic, cadmium, lead and nickel, often present as

impurities or additives in alloys, to contaminate the water. A significant amount of research has been carried out on lead leaching from leaded alloys (Oliphant, 1992). Up until the start of the conormative research, background information was not sufficiently detailed to enable a generalized standard test to be designed.

For materials like stainless steels, the mechanisms are quite different. Corrosion resistance in stainless steels is provided by a passive film that acts as a barrier between the alloy and the water. The passive film is a continuous, non-porous and insoluble film, which, if broken under normal conditions, is self-healing. Due to these characteristics, the uniform corrosion of stainless steels is usually very low and the major risk is pitting corrosion. The pitting corrosion risk of stainless steels is influenced not only by the composition of the alloy and by water quality but also by service conditions, quality of the material and quality of the installation (fitting, soldering conditions, etc.).

Plumbing design The final metal concentration at the tap is not just determined by water quality. Metal release by metal pipes is also strongly influenced by the type of domestic drinking water installation, such as materials and dimensions (length and diameter). The increase in metal concentration with stagnation time varies with the pipe diameter (Kuch *et al*., 1983). For instance for lead pipes, calculated and experimental stagnation curves show that 90 % of the maximum lead concentration is reached after 2 hours for pipes of 10-mm internal diameter but more than 24 hours for pipes of 50-mm diameter.

The plumbing design also includes the number and type of fittings or solder used in the installation and various galvanic couplings. Very little information is available on these subjects.

Ageing of metallic surfaces The corrosion process starts with the chemical reaction between the metal surface and the drinking water and some time is required to develop a corrosion layer with protecting properties on a metal surface. The ageing time of metallic surfaces will differ from one material to the other. For instance, for copper pipes it takes weeks, months, or even years in some cases, depending on the water quality, to develop such a stable film. To get insight into the mechanism of ageing of metallic surfaces, it looks as if it will be necessary to perform (rig) tests over a longer period.

Flow regime As metal concentrations usually increase with time, it seems obvious that metal concentrations in drinking water might vary strongly during the day because of variations in the stagnation time between use of drinking water. Therefore, tap patterns of consumers seem also to be predominant factors in the metal concentration in drinking water at the tap.

In the tap pattern, the mean inter-use time, the volume of water drawn and flow rate all play a role. The water use pattern depends on the household's size, such as the number and age of occupants but also on habits of water usage of the householders (Bailey *et al.*, 1986).

Table 4.1 Inter-use stagnation times for different household sizes (Bailey *et al.*, 1986)

Household size [persons]	Mean [min]	SD [min]
1	47	23
2	29	14
3	24	13
4	22	13
5+	18	6

Table 4.1 gives a summary of the results of a study of the relationship between mean inter-use time and household size.

These results show clearly the great spread in mean inter-use times that can be observed in different households. As metal concentrations rise rapidly in this range of stagnation times, it can be concluded that metal concentrations might vary widely between households.

Existing test protocols

Until now simplified methods have been available to monitor metal release by metallic pipe materials. In the United Kingdom a sit-and-soak test is available to determine the metal release from drinking water materials. In The Netherlands, copper and lead pipes in combination with water quality are tested in pipe rigs, and in Germany a protocol for testing pipe materials is available (see below).

BS 7766: 1994 The procedure given in the British Standard 7766 has been developed to test those alloys for which no direct data as to their service performance is available. BS 7766 was developed to measure the leaching of lead from brass.

The method consists of taking cylindrical test coupons of specified dimensions and surface finish, and suspending them in a specified volume of a specified test solution representative of a moderately aggressive supply water for a period of 24 hours. The immersions are repeated ten times using fresh test solution. Metals are determined using the extract from the final 24-hour period.

Pipe rig tests in the Netherlands In The Netherlands in the mid 1980s a pipe rig was developed and used at several pumping stations to measure lead and copper concentrations in the drinking water. The rig consists of three pipes through which water is flowed continuously except when sampling. The flow rate is about 0.05 m/s. The metal concentration in the drinking water is measured after 24-hour stagnation.

For copper, the rig tests are applied at pumping stations where the water has a high copper solubility. For lead, the rigs are placed at the majority of the pumping stations that deliver water to areas with lead pipes. The results from the pipe rig test show a good correlation with metal concentrations at the tap. The Netherlands government has accepted the pipe rig test for compliance monitoring.

Pipe rig tests in Germany (DIN standard) The German standard DIN 50931-1 went to press at the beginning of 1999. It is the result of intensive mutual interaction between laboratories that are participants in the conormative research project and the German working group, which was establishing a German standard for corrosion tests with drinking water. The exchange of experiences between these two groups resulted in similar testing procedures and protocols. These protocols only differ in nuances.

DIN 50931/1 (1999) describes the design, operation and sampling of a typical plumbing installation for metallic materials testing. In DIN 50931 the last 5 m of a domestic plumbing installation is imitated. In the German Standard DIN 50931, Part 1, an average value calculated from eight samples, which have to be taken after different well-defined stagnation times has been proposed: ½ hour stagnation (×2), 1 hour (×2), 2 hours (×1), 4 hours (×1), 8 hours (×1), 16 hours (×1).

NSF/61 – 1997b test The ANSI/NSF Standard 61 – 1997b (1997) was approved by the American National Standards Institute in September 1997. This test is a short-time sit-and-soak test procedure developed primarily for the testing of products intended for use in drinking-water installations. The standard includes protocols for testing all types of material, instructions for calculating the product dosages from the measured concentrations after defined exposure times, and criteria for rating of acceptable and unacceptable products.

4.2.3 Experiments Within Conormative Research

Introduction

This paragraph describes the test protocols and experimental results for experiments carried out within the conormative research project.

Sit-and-soak tests have been carried out with BS 7766 standard test water and with laboratory tap waters (composition of waters given in Table 4.3). Pipe rig experiments have been carried out with laboratory tap waters, and four materials have been tested: copper, brass (copper with brass fittings for pipe rigs), galvanized steel, and stainless steel.

Materials used for tests were supplied by manufacturers. The same materials coming from the same batches were supplied to each laboratory.

Investigation of a short-term laboratory procedure for assessing the potential of metals to contaminate potable water

Introduction The convenience of having a relatively simple, short-term, laboratory procedure to assess the potential of metals to contaminate potable waters, both for the development of new alloys and in determining any limitations on use of established alloys due to water composition, is self evident. The purpose of the investigations undertaken as part of the conormative project was to determine the ease of achieving reproducibility with such tests, and to consider to what extent the quantitative results reflect the levels of contamination achieved in authentic plumbing systems.

Experimental procedure The experimental procedure used in this part of the project was based on that given in the British Standard BS 7766:1994. This method was used because it is an established procedure with a substantial amount of experimental data and experience behind it, and because it is typical of simple sit-and-soak laboratory procedures.

Details of the method are summarized in Table 4.2. In essence, coupons of the material under test are prepared to defined dimensions and surface finish (the machining is carried out dry, i.e. no lubricating oils, to a surface finish better than 100 μm centre line average, CLA). After a degreasing and washing procedure, the coupons are suspended in the specified test water for 14 days. The test water is changed every 24 hours, except over the two weekend periods, making ten changes altogether. The ambient temperature is controlled throughout the test period at 24 °C. Twenty replicates are run per test and the metal concentrations in the final 24 hour extracts are measured. Five blank samples are run for those days when the concentrations of leachates from the coupons are determined. The blanks are processed in the same way apart from the fact that a test coupon is not suspended in the water. If the blanks show metal levels above the detection limit of the analytical method, the test is void.

Table 4.2 Summary of the laboratory sit-and-soak test procedure (based on BS 7766, 1994)

Test piece	Cylinder 8 mm diameter × 50 mm long 1 mm wide 45° chamfer at each end 2 mm hole 3 mm from one end to suspend sample
Test water	50 mg/l calcium carbonate (dissolved in deionized water) 50 mg/l sodium chloride Total alkalinity = 50 mg/l as $CaCO_3$ pH 7 ± 0.2 adjusted using CO_2 and filtered air
Test conditions	Each cylinder degreased in methylated spirit and washed in test water 20 replicates individually suspended in 100 ml test water held at 24°C Water changed every 24 hours, except over weekends Metal concentrations in test water determined after 14th day (10th change of water)

Experimental programme Initially the materials being used in the pipe rigs, i.e. galvanized steel, stainless steel, copper and brass, were tested by the sit-and-soak procedure. Two sets of tests were carried out, one using the standard test solution given in Table 4.2, and a second using the local water being supplied to the respective pipe rigs in each of the participating laboratories (see Table 4.3). The latter set of tests were carried out in the hope of establishing a correlation between pipe rig results and the laboratory tests.

Because of the difficulty of obtaining a representative surface finish, the original BSI procedure was adapted in the test for galvanized steel. Short sections of pipe, i.d. 21 mm and manufactured to BS 1387: 1985, were cut and the exposed iron and external galvanized surfaces masked using an epoxy paint. The length of pipe cut was calculated to give the same exposed surface area to water volume ratio used in the tests of the other metals, i.e. approximately 13 570 mm^2/l. A short length of glass rod was fixed using an epoxy resin adhesive diametrically across one end of the pipe so that the samples could be suspended above the bottom of their respective beakers during the test.

Because of anticipated difficulties in machining, the stainless steel samples were tested in the form of rectangular bars (50 mm $\times$ 12 mm, thickness = 1.2 mm) rather than cylinders; otherwise the sample geometries were as given in Table 4.2.

When the interest in the procedure progressed to considering interlaboratory reproducibility, a further four sets of tests were carried out using brass samples only. In the last three of these, modifications were introduced into the original procedure; these were:

- the test solution pH adjusted to approx. 8.2;
- the test solution pH adjusted to approx. 8.2 and agitated (using an orbital shaker) during the exposure period;
- the standard test solution, i.e. pH about 7, but the test carried out in an enclosed vessel.

The participating laboratories split into subgroups to carry out these last tests. The reproducibility, both within and between laboratories, was assessed by calculating coefficients of variance and applying a simple *t*-test between means.

Results The results from all these tests are summarized in Table 4.4.

Analysis of reproducibility when using the standard test water: The results for stainless steel were not considered in this part of the programme because the majority of the values for metal leaching were below the analytical detection limits.

A simple *t*-test was carried out on the results between laboratories, and between the results from the same laboratories on the repeat tests, when using the BS test

Table 4.3 Mean composition of laboratory waters supplied to pipe rigs

Laboratory test waters	CRECEP	Kiwa	LHRSP	TZW0	TZW1	TZW2	WRC
Calcium (mg/l)	89.0	72.0	36.0	121.0	60.2	195	13.1
Magnesium (mg/l)	3.2	5.8	6.2	12.0	2.1	24.2	3.7
Sodium (mg/l)	9.2	12.4	16.1	12.6	12.6	12.6	8.8
Potassium (mg/l)	2.3	1.2	2.7	1.8	1.9	1.9	1.5
Bicarbonate (mg HCO_3/l)	223.0	269.1	70.7	328	202.1	435	60.9
Chloride (mg/l)	22.0	9.2	17.0	25.9	17.0	63.8	10.2
Sulphate (mg/l)	25.0	<2.0	66.7	64.0	1.9	146.4	15.4
Nitrate (mg NO_3/l)	21.1	0.62	3.1	31.4	19	34.1	1.7
Phosphate (mg P/l)	—	—	—	—	—	—	0.83
Total hardness (mg $CaCO_3$/l)	236	204	116	351	159	586	48
Total alkalinity (mg $CaCO_3$/l)	183	217	57	269	163.	357	50
pH	7.7	7.7	7.5–8.0	7.2	7.4	7.1	7.5
Total Inorganic Carbon (mg CO_2/l)	169	201	54–50	273	158	374	44
Conductivity (μS/cm)	444	388	310	684	366	1090	—

TZW0 is Karlsruhe tapwater.
TZW1 is Karlsruhe tapwater which has been passed through a nano-filter (filtrate).
TZW2 is the reject water produced when the Karlsruhe tapwater was nano-filtered (concentrate).

Table 4.4 Summary of results of sit-and-soak tests

	Zinc (mg/l)			Lead (μg/l)		
Laboratory	Mean	S.D.	% Covar.	Mean	S.D.	% Covar.
Galvanized steel: BS test water						
CRECEP	2	0.42	21.0	2.65	2	75.5
Kiwa	7.1	3.6	50.1	2.15	1.2	55.8
LHRSP	7.2	2.6	36.6	<10	—	—
TZW	1.71	0.21	12.3	1.00	0.00	2.2
WRc	3.7	0.98	26.5	0.87	0.72	82.8
Galvanized steel: laboratory waters						
CRECEP	1.07	0.39	36.4	5.6	1	17.9
Kiwa	0.80	0.09	11.3	0.78	0.4	51.3
LHRSP	2.08	0.81	39.2	<10	—	—
TZW1	0.94	0.13	13.8	1.7	0.8	47.1
TZW2	1.69	0.19	11.2	3.9	1.3	33.3
WRc	5.13	1.47	28.7	0.94	0.74	78.7

Stainless steel: BS test Water

	Chromium (μg/l)			Nickel (μg/l)			Iron (μg/l)		
	Mean	S.D.	% Covar.	Mean	S.D.	% Covar.	Mean	S.D.	% Covar.
CRECEP	3	0	—	5	2	40	25	6	24
Kiwa	<1	—	—	<1	—	—	<20	—	—
LHRSP	<1	—	—	<1	—	—	<5	—	—
TZW	1	—	—	2.5	0.5	20	10	—	—
WRc	<10	—	—	<10	—	—	4	0	—
Stainless steel: laboratory waters									
CRECEP	<2	—	—	3	2	66.7	33	11	30
Kiwa	<1	—	—	<1	—	—	69	13	18.8
LHRSP	<1	—	—	<1	—	—	4	7	175
TZW1	1.1	0.4	36.4	2.7	0.5	18.5	10	—	—
TZW2	1	—	—	3.9	0.3	7.7	10	—	—
WRc	<10	—	—	<10	—	—	20	3	15

Copper (μg/l)

	BS test water			Laboratory test waters		
	Mean	S.D.	% Covariance	Mean	S.D.	% Covariance
CRECEP	393	80	20.4	390	36	9.3
Kiwa	486	57	11.7	1,485	182	12.3
LHRSP	799	115	14.4	331	80	24.2
TZW	382	54	14.1	—	—	—
TZW1	—	—	—	556	40	7.2
TZW2	—	—	—	912	61	6.7
WRc	254	40	15.7	145	12	8.3

(*continued overleaf*)

Table 4.4 (*continued*)

		Zinc (mg/l)			Lead (μg/l)		
	Test number	Mean	S.D.	% Covariance	Mean	S.D.	% Covariance
Brass: BS test water							
CRECEP	1	1.47	0.16	11.1	95	23	24.9
	2	1.65	0.15	8.8	80.1	11.85	14.8
	3	1.16	0.13	11	30	7	23
	4	0.69	0.07	11	39	5	13
Kiwa	1	1.14	0.12	10.9	51.7	7.25	14.0
	2	0.82	0.07	8.2	74.5	9.05	12.1
	5	1.98	0.35	18	57	5	9
LHRSP	1	0.32	0.11	35	45.0	7.2	16
	2	0.74	0.13	17	42.5	5.88	13.8
	3	1.23	0.17	14	73	13	18
TZW	1	1.54	0.08	5	34.3	2.51	7.3
	2	1.35	0.06	5	39.4	6.96	17.7
	5	2.93	0.10	4	69	4	6
WRc	1	0.68	0.08	11.5	44.2	10.05	22.7
	2	1.14	0.06	4.8	32.5	6.45	19.8
	3	0.93	0.08	8.5	47	11	23
	4	0.83	0.07	9	49	15	30

Brass: laboratory waters

	Zinc (mg/l)			Lead (μg/l)			Copper (μg/l)		
	Lead (μg/l)								
	Mean	S.D.	% Covariance	Mean	S.D.	% Covariance	Mean	S.D.	% Covariance
CRECEP	0.52	0.1	19.2	33	5	15.2	17	3	17.6
Kiwa	2.34	0.78	33.3	95	33	34.7	186	65	34.9
LHRSP	0.88	0.1	11.4	48	5	10.4	37	9	24.3
TZW1	0.92	0.07	7.6	44	1.7	3.9	35	5.1	14.6
TZW2	2.9	0.28	9.7	73	6.4	8.8	116	8.3	7.2
WRc	0.24	0.25	104.2	8.5	8.4	98.8	—	—	—

Key: Tests 1 and 2 = Standard sit-and-soak procedure based on BS 7766:1994.
Test 3 = pH of test water increased to about 8.2.
Test 4 = pH of test water increased to about 8.2 plus agitation during exposure period.
Test 5 = pH of test water at about 7.0 and coupons exposed in an enclosed vessel.

water. The formula for the t-test is as follows:

$$|t| = \frac{(m_1 - m_2).(n_1 + n_2 - 2)}{(\sigma_1^2 - \sigma_2^2)}$$

where $|t| > 2$ for 20 results represents a statistically significant difference;
$m_1 - m_2$ = difference between the population means of the two sets of data
σ_x = standard deviation of the x data set
n_x = number of observations in the x data set

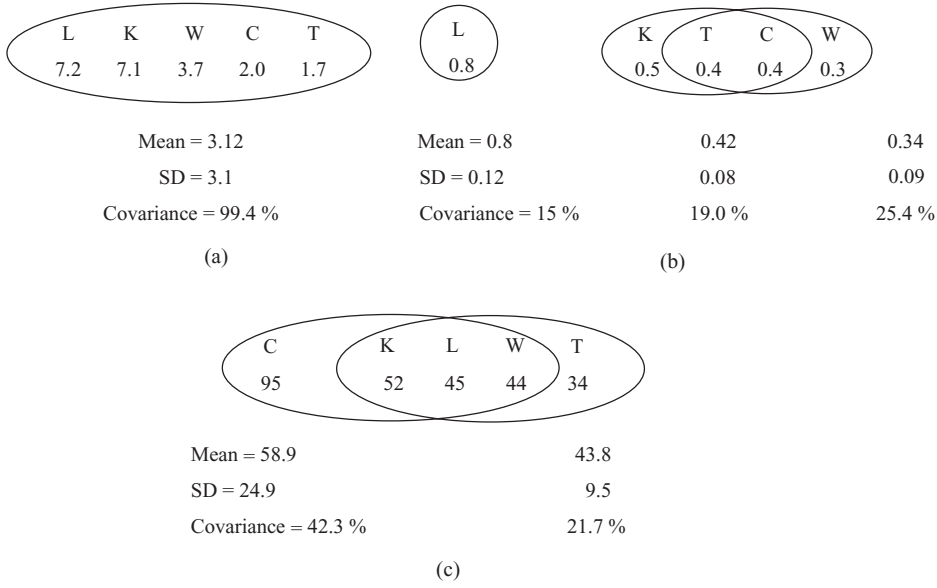


Figure 4.2 Statistically significant groupings (by *t*-test) of inter-laboratory results (C = CRECEP, K = Kiwa, L = LHRSP, T = TZW, W = WRC). (a) *Zn from galvanized (mg/l)*; (b) Cu from copper (mg/l); (c) Pb from brass, Test 1 (mg/l)

The outcome of this analysis is summarized in Figure 4.2 and Table 4.5.

The collective results from the five laboratories for the contamination by Zn from galvanized pipes formed a single group, i.e. there was no statistical difference between the values. However, this was only achieved because the very large scatter between replicates bridged the large difference between means obtained by the different laboratories, see Figure 4.2 (a).

The collective results for Cu contamination from pure copper formed three statistically distinct groups, two overlapping and the highest with LHRSP on its own (Figure 4.2 (b)). The result from LHRSP might be an analytical error on the last

Table 4.5 Statistically significant differences (by *t*-test) between repeat results within the same laboratories for brass tests 1 and 2

	Statistically significant difference between test results?	
Determinand	Pb	Zn
CRECEP	No	No
Kiwa	No	Yes
LHRSP	No	Yes
TZW	No	No
WRc	No	Yes

day's result, a possibility suggested by the much lower values achieved by LHRSP on the earlier days of the test.

The collective results for the contamination of lead from brass obtained from the first set of tests form two overlapping statistical groups (Figure 4.2 (c)). The range of results in the higher statistical group (CRECEP 95 μg/l to WRC 44 μg/l) is wider than that in the lower one (Kiwa 52 μg/l to TZW 34 μg/l). This, and the equivalent results obtained during the development of the original BSI procedure, suggested that it was the CRECEP result that was out of line.

Unfortunately, the lead results from brass in the second set of tests (all laboratories with brass coupons only), where greater care to follow the protocol had been exercised, split into two non-overlapping statistical groups with Kiwa now joining CRECEP in the higher of these. Comparison of the within-laboratory lead results from the two sets of tests showed no statistical difference between them, i.e. each laboratory was able to repeat its results (Table 4.5).

The collective results for the contamination by zinc from brass were even more complicated. The first set of tests produced four distinct statistical groups, two of which were overlapping. WRC and LHRSP both formed statistically distinct groups on their own at the lower end of the range of results. In the repeat experiment, three statistically distinct groups were obtained, none of them overlapping. WRC was still in a group of its own but now this was in the middle of the range.

The within-laboratory comparisons also showed differences with Kiwa, LHRSP and WRC producing statistically distinct sets of results in their repeat tests (Table 4.5).

The collective results for contamination by copper from brass produced two overlapping statistically distinct groups with no obvious candidate for the 'rogue' result. However, all results were very low and would have little practical significance.

Raising the pH of the test solution to its equilibrium value with the atmosphere (Test 3) brought the zinc-from-brass results for the three laboratories concerned into the same statistical population. This was an improvement over any of the previous tests, but the effect was not uniform. Thus, only for CRECEP did raising the pH consistently reduce the zinc contamination level as compared with the previous tests on brass. For LHRSP, the zinc levels were actually increased whereas for WRC the result from test 3 was between those of tests 1 and 2 (see Table 4.4d).

When agitation was introduced (test 4), a statistically significant reduction in the zinc-from-brass level was achieved by CRECEP but not by WRC (see Table 4.4d). However, the two laboratories still remained in the same statistical population (LHRSP did not participate in test 4.)

The results for lead in the same experiments were also not straightforward. The CRECEP and WRC results from test 3 were in the same statistical population with the CRECEP result showing a statistically significant fall from its previous results in tests 1 and 2. However, at the same time the LHRSP result showed a statistically significant rise over its previous tests so that, although it was in the same statistical population as WRC, it was in a different population to that of CRECEP. The introduction of agitation in Test 4 had no statistically significant effect on the lead results for either

Table 4.6 Ranking severity of contamination of metals from brass coupons exposed to the local laboratory waters being supplied to the respective pipe rigs

	CRECEP	Kiwa	LHRSP	TZW1	TZW2	WRc
Lead	5	1	3	4	2	6
Zinc	5	2	4	3	1	6
Copper	5	1	3	4	2	—

1 = highest contamination level, 6 = lowest

CRECEP or WRC. All the lead from brass results for WRC, i.e. from tests 1,2 3 and 4, were in the same statistical population.

Carrying out the extraction process in an enclosed vessel (test 5) to prevent the loss of free CO_2 in the pH 7 test solution, produced a statistically significant increase in the amount of zinc extracted (Table 4.4d). In open beakers, the pH increases (up to about 8) during the 24-hour period because of the loss of free CO_2, whereas this phenomenon does not occur in enclosed vessel where the pH remains lower. As zinc solubility decreases when pH increases, the differences between test 1 (open beakers) and test 5 (enclosed vessel) are consistent with the theory. Unfortunately, the results from the two laboratories concerned, Kiwa and TZW, were not in the same statistical populations. Slight differences in start pH (tolerance in BS 7766 is 7.0 ± 0.2) could explain this difference.

The lead results from the two laboratories were in the same statistical population and for TZW was significantly higher than the corresponding results in tests 1 and 2. The Kiwa lead result in test 5 was only statistically significantly different from their test 2 result (Table 4.4d).

Results with the laboratory pipe rig waters: Because of the different water qualities, it was obviously not possible to study the reproducibility of the results from the tests that used the different laboratory waters being supplied to the respective pipe rigs. However, it was possible to make a few generalizations.

The order of 'severity of contamination' by Zn, Pb and Cu from brass with the different laboratory test waters were approximately the same, for example, the water that is worst for Pb was also worst for Cu and second worst for Zn (Table 4.6).

The order of 'severity of contamination' by Cu from copper and Cu from brass in the different laboratory test waters was also similar although the absolute levels were very different (Table 4.7).

Table 4.7 Comparison of the ranking severity of contamination by copper leached from pure copper and brass coupons exposed to the local laboratory waters being supplied to the respective pipe rigs

	CRECEP	Kiwa	LHRSP	TZW1	TZW2	WRC	Mean (μg/l)
Cu from copper	4	1	5	3	2	6	635
Cu from brass	5	1	3	4	2	—	78

1 = highest contamination level, 6 = lowest

Table 4.8 Materials used in rig experiments

Material tested	Pipe material	Internal diameter (mm)	Fittings	Rig volume (litres)
Copper	Copper, hard drawn	13	None (bent copper)	0.67
Brass[a]	Copper, hard drawn	13	Brass (63.6 % Cu, 1,58 % Pb, O.1 % Sn, 34.7 % Zn)	0.67
Galvanized steel	Galvanized steel (Pr EN 10240)	20	Galvanized steel	1.6
Stainless steel	Stainless steel AISI 304 / 1.4301 (18 % Cr, 9.2 % Ni)	20	Stainless steel AISI 316 / 1.4401 (17 % Cr, 10.6 % Ni, 2.1 % Mo)	1.6

[a] The total inner surface of the brass fittings is 128 $cm^2 \pm 10$ % which represents about 6.5 % of the total inner surface of the test rig.

Reference rig experiments

Experimental procedure The experimental procedure for pipe rig tests is related to the German standard DIN 50931, Part 1 (see above).

The general philosophy of the test was to simulate an 'average authentic situation' representing operating conditions in a *domestic* plumbing system.

Actually, pipe rigs reproduce the final part of domestic plumbing just before a tap.

Design of rigs: Materials used for rigs and their main characteristics are given in Table 4.8. Figure 4.3 gives a schematic illustration of pipe rig design for each material. For each material, all laboratories received pipes and fittings 'ready to install' from the same manufacturers. For copper rigs, the pipes were prepared (bent) by the manufacturer. For stainless steel, rigs were assembled (press fittings) in all laboratories by a technician appointed by the manufacturer. For galvanized steel and copper with brass fittings, pipes and fittings were delivered to the laboratories, which assembled the rigs by themselves.

Materials were used for experiments without any preconditioning.

Rigs were connected to the laboratory water supply (after water treatment by nanofiltration, at TZW). The test device included equipment (valves, solenoid valves plus programming system, flow meter, sampling valves, etc.) for the adjustment and control of flow regime and for water sampling (Figure 4.4).

The test pipes were installed in a vertical position and were always under pressure.

Flow regime: The flow regime was designed to simulate authentic conditions at a kitchen tap. A total volume of 125 litres was flushed every day with alternate stagnation and flushing periods. Figure 4.5 presents the flow regime for a 24-hour period.

Flushing times were of 1 or 2 minutes at a flow rate of 300 litres per hour, which gives a volume of 5 or 10 litres for each flushing period.

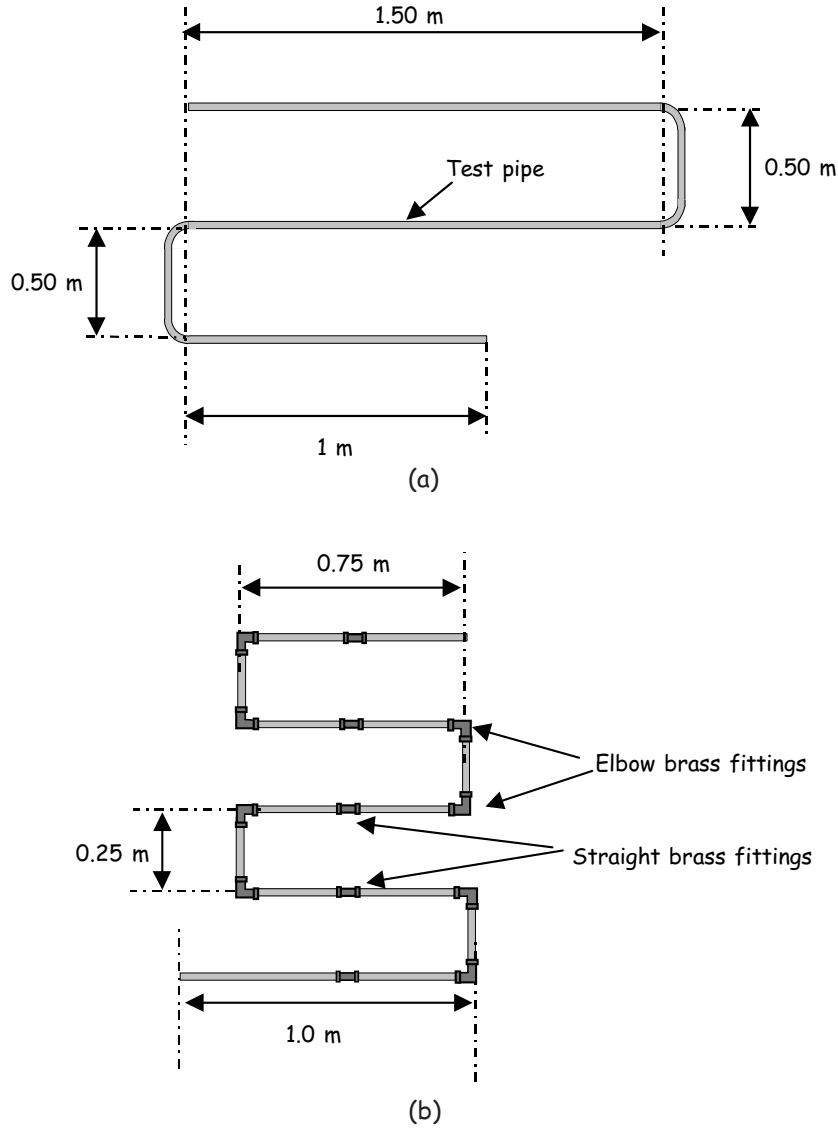


Figure 4.3 Design of test rigs. (a) Pipe materials (copper, galvanized steel, stainless steel); (b) copper pipe with brass fittings

Sampling procedure: Before sampling water for analysis, a small volume of water (approx. 100 ml) was flushed to waste in order to rinse the sampling device and the first few centimetres of the pipe. Then samples of water that had stagnated in contact with the material were taken for analysis. The sampling programme adopted for the first five months of test run was as follows:

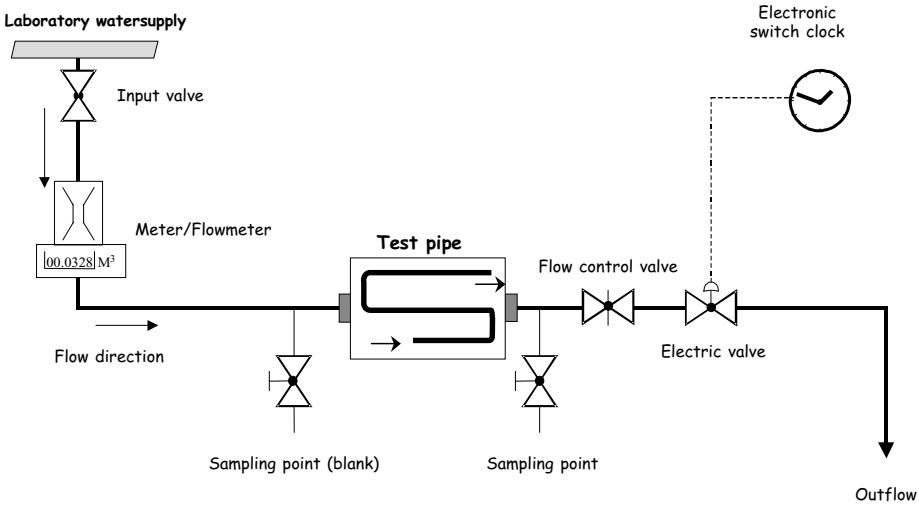


Figure 4.4 Example of test device for pipe rig experiments

Half hour stagnation samples:

- 1st month: samples taken on days 1, 3, 6, 12 and 24.
- Months 2 to 5: Samples were taken each month over five consecutive days. The five samples could then be combined for analysis of an average sample or be analysed separately to calculate the mean concentration.

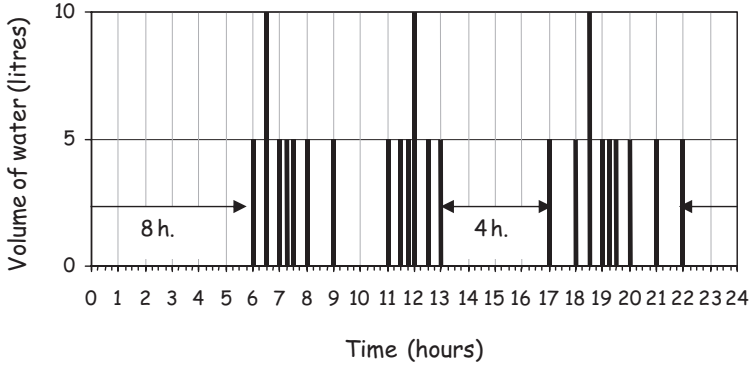


Figure 4.5 Flow regime in pipe rigs for a 24-hour period. Stagnation periods are:15 minutes (6), 30 minutes (9), 1 hour (4), 2 hours (1), 4 hours (1), 8 hours (1) (overnight stagnation)

Stagnation curves:

During months 2 to 5 of the run, stagnation curves for the metals of interest were constructed. This involved taking individual ½, 2, 4 and 8 hour stagnation samples.

The sampling programme was adapted, on behalf of each laboratory, according to observed results and tendencies in contamination by metals. When necessary, test runs were prolonged after the initial 5-month periods and 1 hour and/or 16 hour stagnation samples were taken.

Analysis: pH and metal concentrations were determined in each sample at all stagnation times. Dissolved oxygen was measured for stagnation times of 1 hour or longer (and optionally for ½ hour). Metal concentrations were measured in filtered and non-filtered samples in order to distinguish between soluble and particulate metal.

The list of metals depends on the material:

- Copper: Cu
- Brass: Cu, Zn, Pb
- Galvanized steel: Zn, Pb (and occasionally Cd)
- Stainless steel: Fe, Ni, Cr

Experimental results

Copper: Results for copper are summarized in Table 4.9 and Figure 4.6.

Figure 4.6 presents smoothed 3D plots of copper concentration as a function of stagnation time and operating time for the different test waters. These graphs were calculated from actual data, and they show the main tendencies in the evolution of copper release but 'peaks' were erased by calculation.

(a) Stagnation curves ([Cu] = f(stagnation time)). Copper concentration always increase for stagnation time up to 8 hours. CRECEP and TZW performed extra experiments with 16-hour stagnation. For CRECEP and TZW nanofiltration filtrate, Cu concentration still increased between 8 and 16 hours. For TZW tap water and nanofiltration concentrate a maximum was reached between 8 and 16 hours, and concentration generally decreased after 8-hour stagnation. In these cases, the maximum copper concentration was correlated with a minimum dissolved oxygen concentration. In fact, strong oxygen depletion was observed with stagnation time for TZW tap water and nanofiltration concentrate.

Oxygen depletion with stagnation time was also observed with other test waters but not in the same range. High oxygen consumption indicates high corrosion rates and often results in high copper concentrations.

(b) Ageing ([Cu] = f(operating time)). The shape of the evolution of copper concentrations with operating time can be described by three types of curve:

Type 1: 'exponential' decrease to a minimum value;

Type 2: increase to a plateau value;

Table 4.9 Copper concentrations in copper rig experiments at different stages. Bold characters: Copper concentration >1 mg/L

Stagnation time	*a*	CRECEP	KIWA	LHRSP	WRC	TZW Concentrate	TZW Filtrate	TZW Tap
½ hour	Max (*day*)	0.33 (*134*)	0.82 (*14*)	0.14 (*24*)	0.39 (*2*)	**4.2 (*819*)**	0.56 (*27*)	**1.5 (*336*)**
	Min (*day*)	0.07 (*263*)	0.15 (*7*)	0.008 (*578*)	0.016 (*5*)	0.56 (*5*)	0.04 (*588*)	0.39 (*5*)
	Mean (*SD*)	0.17 (*0.09*)	0.46 (*0.11*)	0.06 (*0.01*)	0.038	**1.67 (*0.37*)**	0.09 (*0.01*)	**1.3 (*0.1*)**
2 hours	Max (*day*)	0.97 (*75*)	2.3 (*30*)	0.21 (*54*)		**11 (*819*)**	**1.1 (*27*)**	**3.4 (*236*)**
	Min (*day*)	0.22 (*324*)	0.53 (*270*)	0.03 (*578*)		**2.52 (*90*)**	0.08 (*588*)	**2.0 (*5*)**
	Mean (*SD*)	0.42 (*0.18*)	**1.2 (*0.4*)**	0.13 (*0.03*)	0.12	**4.6 (*0.9*)**	0.18 (*0.03*)	**3.2 (*0.3*)**
4 hours	Max (*day*)	**1.55 (*75*)**	**3 (*30*)**	0.39 (*54*)		**13.7 (*792*)**	**1.9 (*5*)**	**8.4 (*139*)**
	Min (*day*)	0.33 (*324*)	0.83 (*90*)	0.034 (*578*)		**3.9 (*69*)**	0.10 (*819*)	**3.25 (*728*)**
	Mean (*SD*)	0.59 (*0.25*)	**1.6 (*0.5*)**	0.2 (*0.06*)	0.17	**7.4 (*1.5*)**	0.24 (*0.04*)	**5.6 (*1.0*)**
8 hours	Max (*day*)	**2.5 (*76*)**	**3.4 (*30*)**	0.5 (*54*)		**17 (*792*)**	**2.7 (*5*)**	**9.3 (*139*)**
	Min (*day*)	0.5 (*364*)	**1.1 (*90*)**	0.05 (*578*)		**7 (*69*)**	0.10 (*819*)	**3.3 (*728*)**
	Mean (*SD*)	0.84 (*0.39*)	**2.1 (*0.7*)**	0.34 (*0.10*)	0.09	**11 (*2*)**	0.34 (*0.07*)	**7.5 (*1.4*)**

[a] Max (*day*) = maximum concentration at given stagnation time (*corresponding operating time*).
Min (*day*) = minimum concentration at given stagnation time (*corresponding operating time*).
Mean (*SD*) = mean concentration for days 100 to 300 (*standard deviation*).

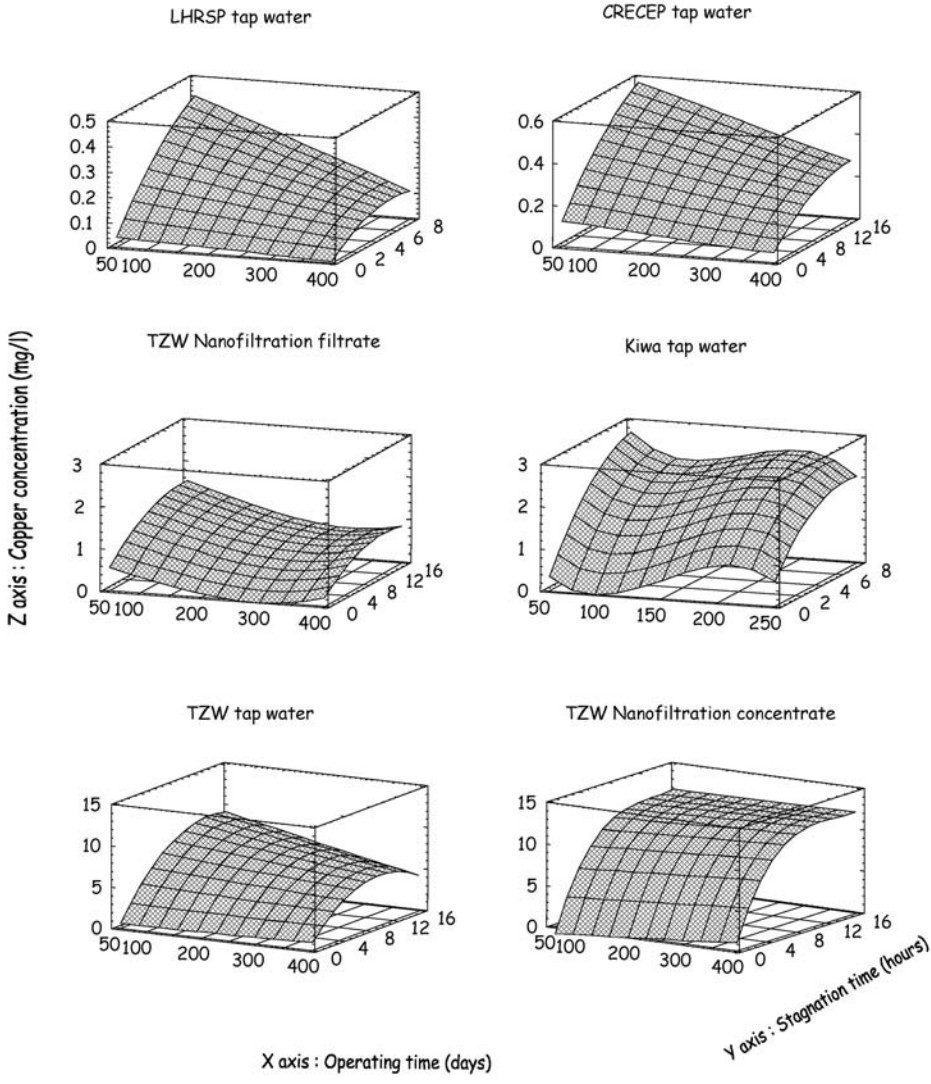


Figure 4.6 Copper rig experiments. Copper concentrations as function of stagnation time and operating time

Type 3: 'peak contamination' after an initial period of low values followed by 'exponential' decrease to a minimum value.

Type 1 or type 3 can describe results from CRECEP, TZW nanofiltration filtrate, WRC, Kiwa and LHRSP. Peak contamination (type 3) appeared in the first weeks in 30-minute stagnation samples (no data exist for longer stagnation times during the first month). After about 2 months' operation, copper concentrations decreased to a minimum with some variation which could be explained (probably) by changes in water quality (pH, temperature, oxygen, etc.).

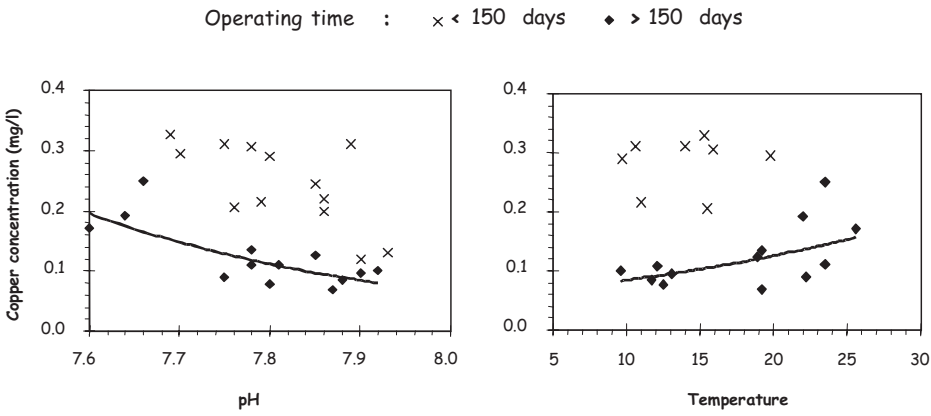


Figure 4.7 Relationship between copper concentration after 30 minutes' stagnation, pH and temperature. Results with CRECEP tap water

The effect of tap water quality is illustrated in Figure 4.7, which shows the relationship between pH and copper or temperature and copper with CRECEP water (values measured during pipe rig experiments). The figure shows that when copper corrosion is 'stabilized' (>150 days operation), variations in copper concentration may be explained by pH and temperature fluctuations.

For TZW nanofiltration concentrate and tap water, type 2 and type 1 were observed depending on stagnation time (Figure 4.6). For tap water, continuous increase (type 2) was observed for 30 minutes' to 2-hours' stagnation, and (slow) exponential decrease (type 1) was observed for longer stagnation times (4 to 16 hours). For the concentrate, the contamination level increased continuously up to 500 days' operation at any stagnation time and stabilised or started decreasing slowly afterward.

For all waters, large changes in copper concentrations were observed in the first 2 or 3 months of operation. After this initial period, changes were generally slower and more continuous but may be significant over long periods of time.

(c) Copper concentrations – water corrosivity. Table 4.9 gives minimum and maximum copper concentrations at 0.5, 2, 4 and 8 hour stagnation for all laboratories, and the mean concentration between day 100 to 300 (to allow comparisons between the laboratories).

TZW nanofiltration concentrate and tap water appeared to be very corrosive waters for copper with concentrations exceeding 3 mg/l after 2-hours' stagnation. With these waters, contamination by copper quickly increased in the first months of operation and then stabilised or started to decrease.

For other waters, after few weeks' operation, copper concentrations always decreased to a minimum value. In the first weeks of operation the changes were more complex and often started with an initial increase (peak contamination).

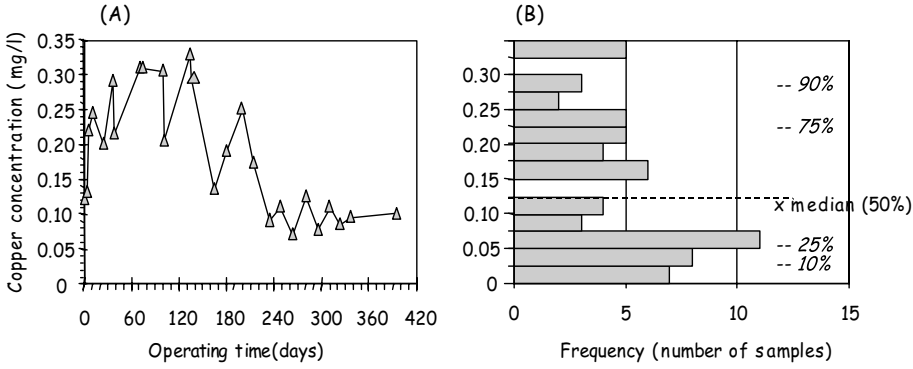


Figure 4.8 Comparison of copper concentrations after a stagnation of ½ hour in CRECEP rig experiments (A) with values observed at consumers' taps (B)

For WRC water (soft water with orthophosphate dosing), initial decrease occured in the very first days of operation and a minimum low level was reached after only 1 or 2 weeks.

In order of decreasing corrosivity, ranking of waters is as follows: TZW concentrate $\gg$ TZW tap $\gg$ Kiwa > CRECEP > LHRSP $\sim$ TZW filtrate > WRC.

(d) Comparison of copper rig results with concentrations measured at consumers' taps. In Paris, between June 1997 and June 1999, 63 samples were taken at consumers' taps and copper concentrations were measured. The samples (2 litres) were taken after a fixed fixed stagnation of ½ hour. Figure 4.8 shows a comparison of copper concentrations measured in copper rig experiments after ½ hour of stagnation with values measured at the tap.

The comparison shows that there is good agreement between copper-rig results and actual copper concentrations at the tap. The median value from field experiments (0.125 mg/l) is very close to the range of copper concentrations found in the rig experiments after 'stabilization' (0.07 to 0.13 mg/l).

The scattering of field results can be explained by the variety of situations encountered in actual plumbing systems (diameters and lengths of copper pipes, age, other materials in the plumbing system, etc.). However this comparison indicates that in this case (CRECEP tap water, copper, ½-hour stagnation samples), the pipe-rig experiments are representative of actual contamination levels.

Copper with brass fittings:

(a) Copper. Contamination by copper followed the same general changes as in the copper-rig experiments. Concentration levels were usually the same in both experiments. However, Figure 4.9 shows that copper concentrations were sometimes lower in copper with brass fitting rigs than in copper rigs. This is very

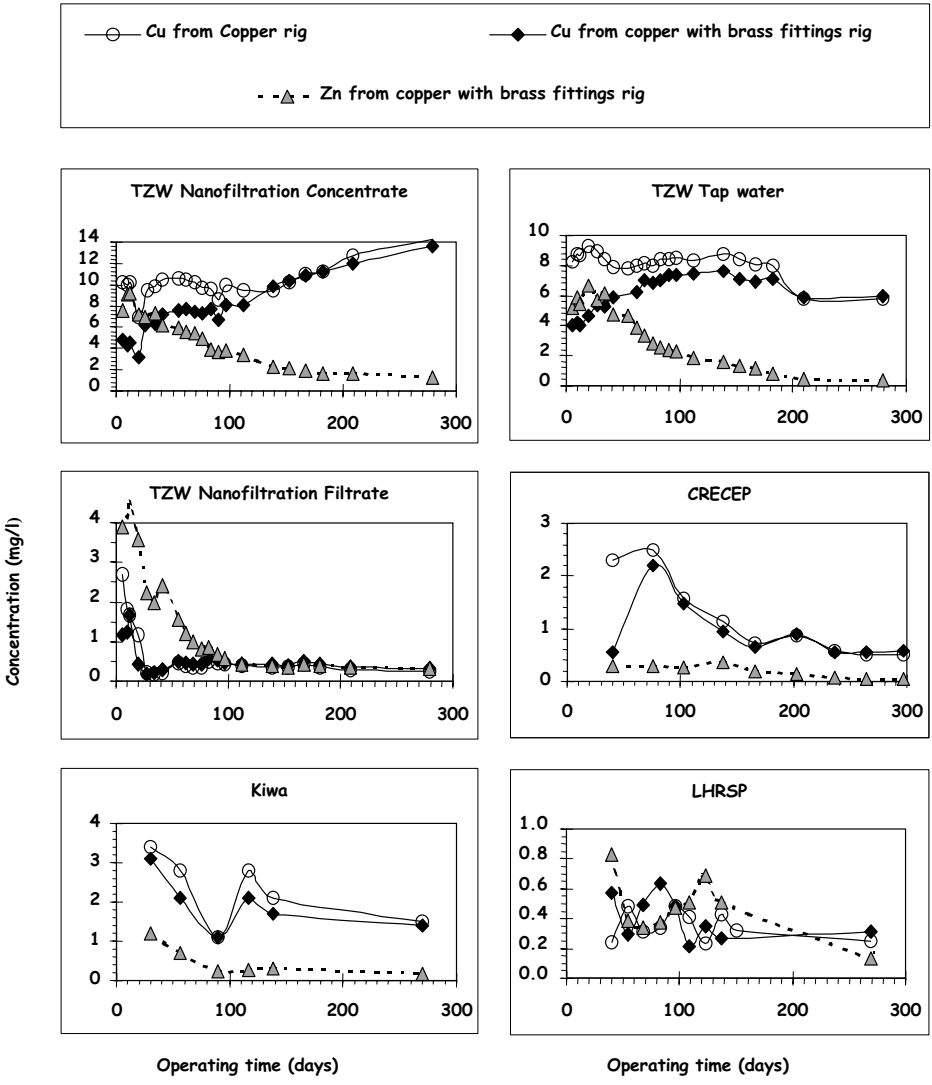


Figure 4.9 Comparison of copper concentrations after 8-hours' stagnation in copper rig and copper with brass fittings rig experiments

clear with the most corrosive waters (TZW filtrate and TZW tap water) in the first months of operation, but it was also observed with other waters. The difference between the two curves was reduced progressively with time until they overlapped almost perfectly. The time period over which differences were observed correlated very well with high zinc concentrations (which, over the same period, exhibited an exponential decrease to a minimum value). This is consistent with other observations that show that zinc can act as a corrosion inhibitor for copper.

The main conclusion from these results is that fitting materials can influence the corrosion rate and behaviour of the pipe materials even if the phenomenon is only temporary (a few days to several months in this case).

(b) Zinc. Results for zinc are summarized in Table 4.10 and Figure 4.10. Zinc is, with copper, a major constituent of brass, and all the results show that zinc is leached in water at significant concentrations with all test waters, where zinc concentrations increased with stagnation times up to 8 hours.

The evolution with operating time followed a type 1 curve (exponential decrease to a minimum value) for all stagnation periods. However, as for copper, variations were observed in the first weeks of operation with, sometimes, peak contamination after an initial period of low values (TZW concentrate, tap water and filtrate, Kiwa).

Very high zinc concentrations (>4 to 9 mg/l) were observed after 8 hours' stagnation with TZW waters (nanofiltration concentrate, filtrate and tap water) but contamination quickly decreased in the first weeks of operation. With other waters, concentrations were lower and did not exceed 1 mg/l even for 8-hours' stagnation. In order of decreasing corrosivity, ranking of waters was as follows: TZW concentrate $\gg$ TZW tap > TZW filtrate > Kiwa $\sim$ LHRSP $\sim$ CRECEP $>\sim$ WRC.

However, it must be noted that after 100 to 200 days, TZW filtrate, Kiwa LHRSP and CRECEP reached 'low' contamination levels in the same concentration range (0.1 to 0.5 mg/l after 8 hours' stagnation) with slow asymptotic decreases there after.

(c) Lead. High lead concentrations (>50 μg/l) were observed with TZW concentrate and TZW tap water in the first days of operation for long stagnation times (>4 hours). Contamination levels quickly decreased in the first days or first week to reach values of less than 10 μg/l in all cases after less than 1 month of operation.

For other test waters the same initial decrease was observed (no data for stagnation over 30 minutes in the first month) in the first weeks of operation. However, initial concentrations did not generally exceed 10 μg/l. After the initial period (10 to 50 days), lead concentrations stabilized at below 5 μg/l and remained at low levels (near analytical detection limits).

For CRECEP, values between 5 and 10 μg/l were observed, but lead was also detected in the blank at the same level. In that case, a small, variable contamination by lead comes from materials before the rigs (a few centimetres of galvanized steel, and brass devices) and cannot be imputed to contamination from brass fittings.

Galvanised steel:

(a) Zinc. Results for zinc are summarized in Table 4.11 and Figure 4.11. With all test waters significant zinc concentrations were detected even after 30 minutes' stagnation and prolonged operating times. Zinc concentrations increased with

Table 4.10 Zinc concentrations in copper with brass fittings rig experiments at different stages

Stagnation time	*a*	CRECEP	Kiwa	LHRSP	WRC	TZW Concentrate	TZW Filtrate	TZW Tap
	Max (*day*)	0.12 (*1*)	0.32 (*14*)	0.20 (*1*)	0.2 (*1*)	1.2 (*34*)	1.13 (*34*)	1.04 (*34*)
½ hour	Min (*day*)	0.01 (*296*)	0.005 (*92*)	0.02 (*6*)	0.03 (*86*)	0.07 (*728*)	0.02 (*792*)	0.04 (*244*)
	Mean (*SD*)	0.04 (*0.02*)	0.01 (*0.008*)	0.06 (*0.03*)	0.038	0.15 (*0.05*)	0.04 (*0.01*)	0.09 (*0.05*)
	Max (*day*)	0.26 (*39*)	0.72 (*28*)	0.30 (*40*)		2.52 (*10*)	1.53 (*20*)	1.74 (*55*)
2 hours	Min (*day*)	0.01 (394)	0.07 (*287*)	0.045 (*269*)		0.12 (*279*)	0.04 (*819*)	0.08 (*427*)
	Mean (*SD*)	0.06 (*0.03*)	0.09 (*0.03*)	0.16 (*0.09*)	0.25	0.5 (*0.2*)	0.14 (*0.04*)	0.28 (*0.14*)
	Max (*day*)	0.47 (*39*)	1.1 (*28*)	0.62 (*40*)		4.83 (*20*)	2.35 (*20*)	3.09 (*27*)
4 hours	Min (*day*)	0.02 (*296*)	0.11 (*287*)	0.095 (*269*)		0.21 (*728*)	0.05 (*755*)	0.10 (*391*)
	Mean (*SD*)	0.10 (*0.08*)	0.15 (*0.03*)	0.28 (*0.16*)	0.43	1.1 (*5*)	0.23 (*0.03*)	0.6 (*0.4*)
	Max (*day*)	0.36 (*138*)	1.2 (*28*)	0.83 (*40*)		9.24 (*12*)	4.48 (*12*)	6.71 (*20*)
8 hours	Min (*day*)	0.04 (*325*)	0.17 (*287*)	0.13 (*269*)		0.34 (*728*)	0.09 (*700*)	0.15 (*700*)
	Mean (*SD*)	0.16 (*0.12*)	0.24 (*0.06*)	0.4 (*0.2*)	0.40	2.1 (*0.9*)	0.39 (*0.07*)	1.1 (*0.7*)

[a] Max (*day*) = maximum concentration at given stagnation time (*corresponding operating time*).
Min (*day*) = minimum concentration at given stagnation time (*corresponding operating time*).
Mean (*SD*) = mean concentration for days 100 to 300 (*standard deviation*).

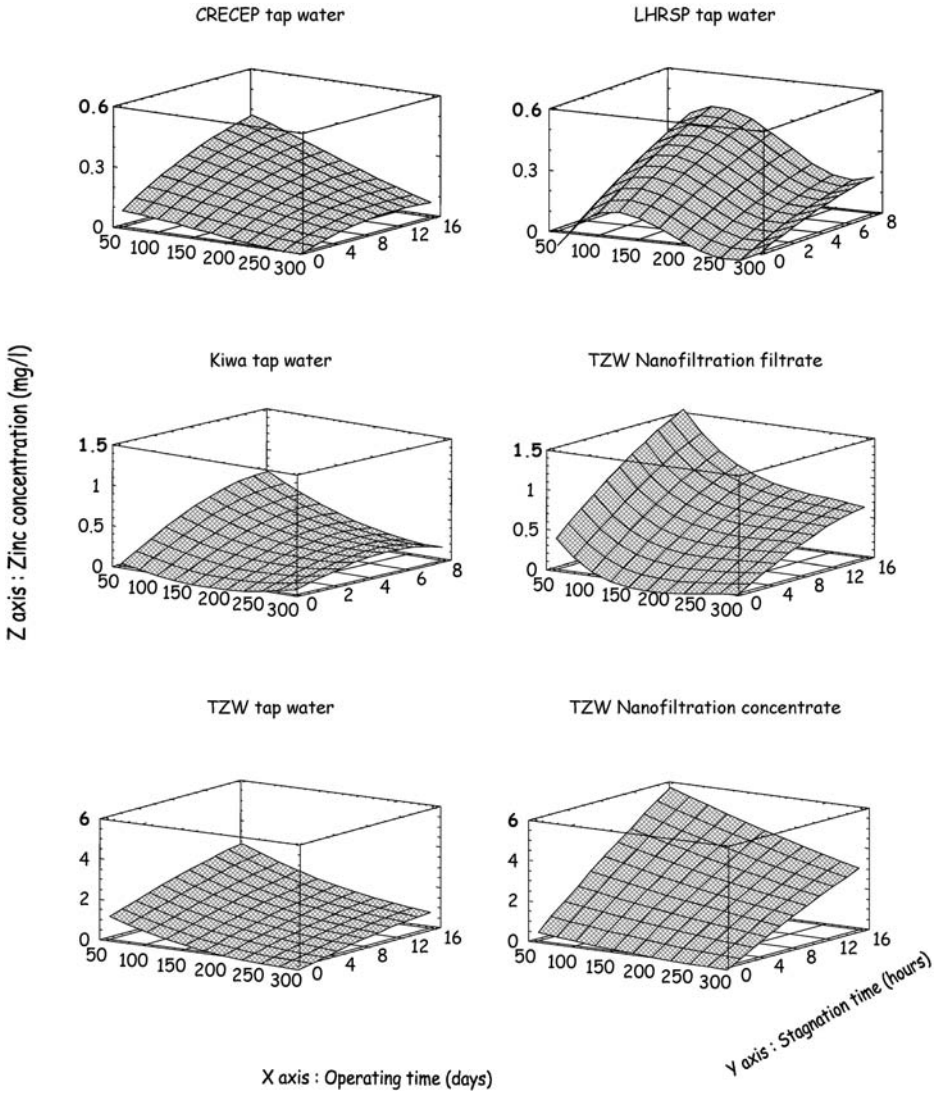


Figure 4.10 Copper with brass fittings rig experiments. Zinc concentrations as function of stagnation time and operating time

stagnation times up to 8 hours in all cases. Experiments carried out with longer stagnation (16 hours: CRECEP, TZW nanofiltration filtrate and concentrate) showed that, generally, the concentration still increased between 8 and 16 hours but tended to stabilize to a plateau or sometimes to decrease slightly (nanofiltration filtrate).

Oxygen depletion was observed in correlation with high zinc concentrations (high corrosion rate), in particular with TZW nanofiltration filtrate and

Table 4.11 Zinc concentrations in galvanized steel rig experiments at different stages

Stagnation time	*a*	CRECEP	KIWA	LHRSP	WRC	TZW Concentrate	TZW Filtrate
½ hour	Max (*day*)	0.45 (*1*)	0.75 (*1*)	1.0 (*1*)	5.6 (*2*)	4.5 (*336*)	2 (*34*)
	Min (*day*)	0.13 (*363*)	0.47 (*270*)	0.10 (*342*)	0.83 (*5*)	0.77 (*519*)	0.76 (*637*)
	Mean (*SD*)	0.24 (*0.06*)	0.50 (*0.04*)	0.19 (*0.08*)	1.6	2.1 (*0.4*)	1.04 (*0.08*)
2 hours	Max (*day*)	0.95 (*200*)	1.9 (*56*)	0.69 (*54*)		14.3 (*336*)	5.1 (*34*)
	Min (*day*)	0.40 (*296*)	1.2 (*270*)	0.26 (*269*)		2.3 (*519*)	2.2 (*264*)
	Mean (*SD*)	0.58 (*0.18*)	1.6 (*0.4*)	0.41 (*0.10*)	0.67	6.6 (*1.8*)	3.2 (*0.3*)
4 hours	Max (*day*)	1.03 (*75*)	2.9 (*56*)	1.6 (*40*)		19.6 (*336*)	7.8 (*5*)
	Min (*day*)	0.57 (*296*)	1.9 (*270*)	0.35 (*578*)		3.7 (*552*)	3.0 (*364*)
	Mean (*SD*)	0.83 (*0.17*)	2.2 (*0.3*)	0.59 (*0.17*)	3.2	9.7 (*2.1*)	4.7 (*0.5*)
8 hours	Max (*day*)	1.8 (*302*)	3.8 (*56*)	1.6 (*54*)		22.4 (*819*)	8.1 (*27*)
	Min (*day*)	0.88 (*297*)	2.7 (*270*)	0.47 (*342*)		5.1 (*90*)	3.4 (*588*)
	Mean (*SD*)	1.3 (*0.3*)	3.3 (*0.5*)	1.0 (*0.3*)	5.66	14 (*3*)	5.6 (*0.7*)

[a] Max (*day*) = maximum concentration at given stagnation time (*corresponding operating time*).
Min (*day*) = minimum concentration at given stagnation time (*corresponding operating time*).
Mean (*SD*) = mean concentration for days 100 to 300 (*standard deviation*).

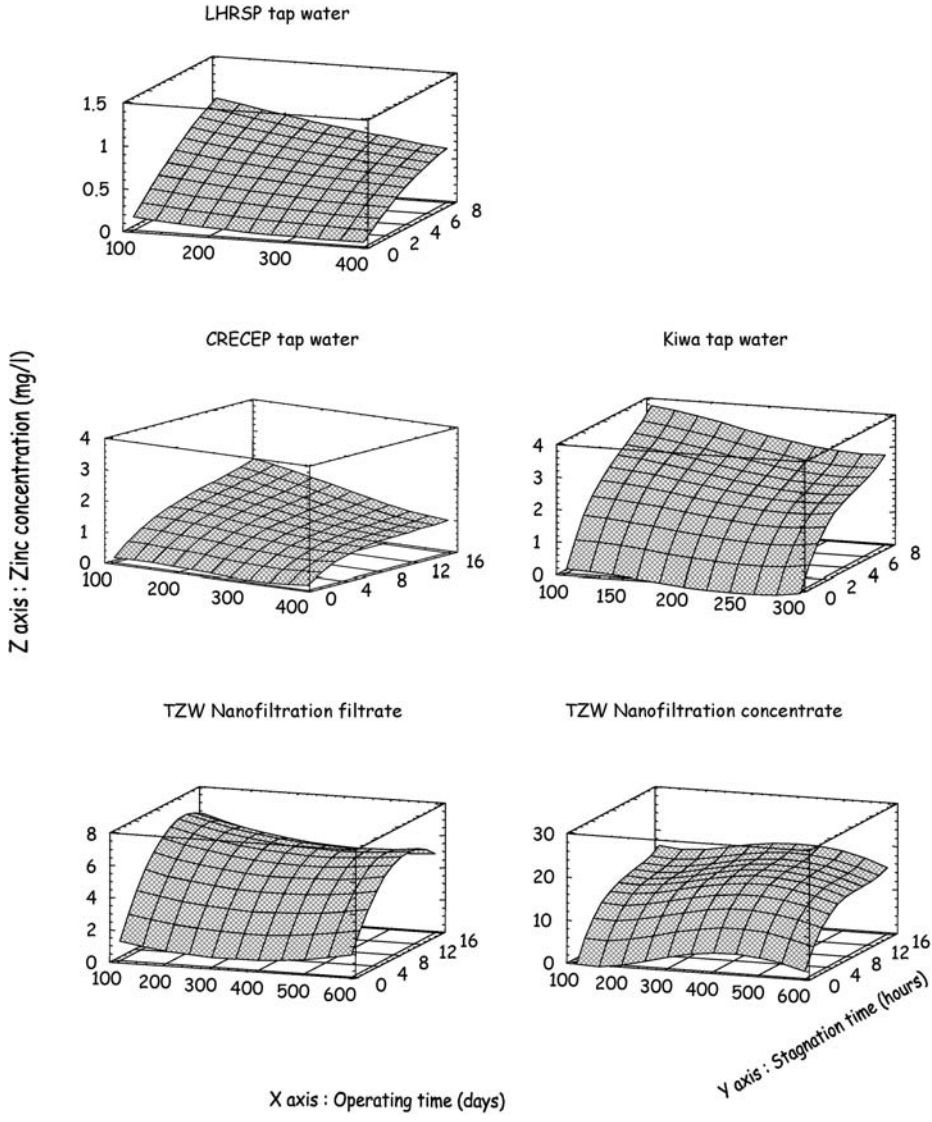


Figure 4.11 Galvanized steel rig experiments. Zinc concentrations as function of stagnation time and operating time

concentrate, where oxygen concentration fell below 1 or 2 mg/l after 8 or 16 hours' stagnation. In the same cases, a slight pH increase could also be observed.

Except with TZW nanofiltration concentrate, zinc concentrations always decreased with operating time, the curves being typically of type 1 (exponential decrease to a minimum value). The maximum levels of contamination occurred

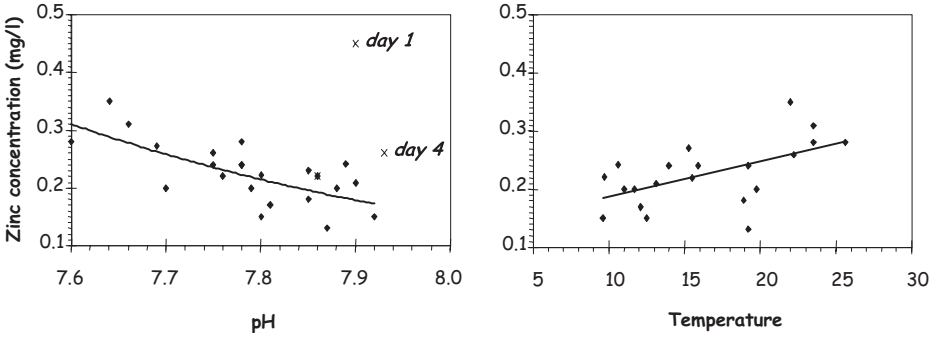


Figure 4.12 Relationship between zinc concentration after 30 minutes' stagnation, pH and temperature. Results with CRECEP tap water

in the first days of operation and were followed by a slow asymptotic decrease with variations, probably due to changes in water quality, over several months.

Figure 4.12 illustrates the relationship between zinc concentration (stagnation of 30 minutes), pH and temperature with CRECEP water. The figure shows that zinc migration was well correlated with pH and temperature, and that small changes in these parameters may significantly affect the contamination level.

The shape of the ageing curves ([Zn] $= f$(operating time)) was different with TZW nanofiltration concentrate and cannot be described by a simple shape (type 1, 2 or 3). Figure 4.13 shows a comparison between the evolution of zinc concentration (after 8 hours' stagnation) and pH of water. Parallel evolution can be seen: an increase in pH corresponds to a decrease in zinc. Thus, it appears very likely that variations in zinc concentration is due essentially to changes in water quality (pH, but probably also temperature, oxygen or other parameters) and not (only?) to ageing of the material.

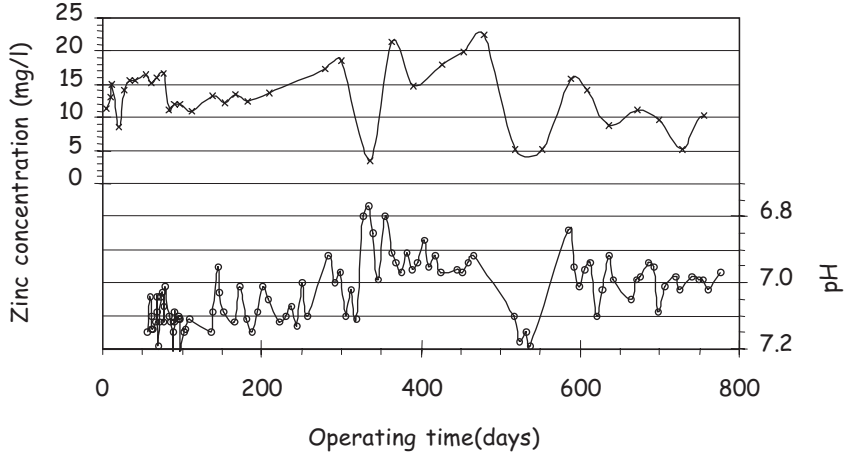


Figure 4.13 Comparison of zinc and pH evolution with operating time for galvanized steel rig with TZW nanofiltration concentrate water

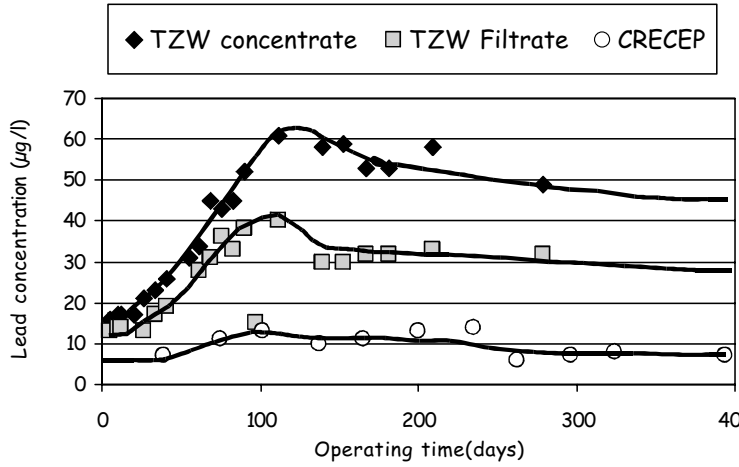


Figure 4.14 Lead concentrations after 8 hours of stagnation as a function of operating time for galvanized Steel rig experiments

In order of decreasing corrosivity, ranking of waters is as follows: TZW concentrate ≫ TZW filtrate ≫ Kiwa > CRECEP > LHRSP.

For WRC, important differences were observed between filtered (dissolved metal) and nonfiltered (total) samples. Particulate metal (total dissolved) represents an important ratio of the total (>50 %). Looking at total metal concentrations up to day 103, WRC should be ranked as TZW filtrate. TZW concentrate and filtrate led to very high zinc concentrations, exceeding 1 mg/l after 30 minutes' stagnation and 5 mg/l after 8 hours (Table 4.11).

(b) Lead. Lead concentrations significantly exceeding 10 µg/l appear only with TZW nanofiltration filtrate and concentrate after 2 hours' stagnation or more.

Values around 10µg/l were also detected with CRECEP water after 8 or 16 hours' stagnation (Figure 4.14).

Results from TZW show that contamination by lead increased continuously in the first months of operation (from day 0 to 100) up to a maximum and then decreased slowly. The maximum level of lead after 8 hours' stagnation was near 60 µg/l for concentrate and 40 µg/l for filtrate during several weeks in both cases. The level of 10 µg/l was frequently exceeded after 1 hour's stagnation. For WRC, even when high (particulate) zinc concentrations were observed, lead remained at low levels (<5 µg/l) and only particulate lead was detected.

These results show that lead is not leached from galvanized steel under the same conditions as is zinc. Migration of lead started only after an initial period of low migration ('induction period') and decreased after a period of high concentration. The induction period was several months with waters of high corrosivity in which high quantities of zinc were leached into the water. With other test waters of lower corrosivity, an increase in lead migration after long operating times cannot be excluded.

Stainless steel: Chromium, nickel and iron have been analysed. For iron, all results were very low and most of them are near detection limits or do not significantly differ from the noise (iron in the test waters). For chromium, all results were below the detection limits of the analytical methods except for one: 25 μg/l after 1 hour's stagnation on day 637. These were both with TZW nanofiltration concentrate.

For nickel, only two results exceeded 10 μg/l: 16 μg/l after 30 minutes' stagnation on day 69, 37 μg/l after 1 hour's stagnation on day 637, both with TZW nanofiltration concentrate. These isolated points cannot be interpreted as real contamination from the material, as all other results were below 5 μg/l.

However, with TZW concentrate, concentrations of between 1 and 5 μg/l were observed, mainly in the first days of operation (with no relation to stagnation time).

4.2.4 Discussion

Achieving reproducibility with a laboratory sit-and-soak test

There are broadly two aspects to determining the reproducibility of a test procedure, which are the ease with which a laboratory can consistently carry out the procedure, and the sensitivity of the results to slight variations in that procedure. Obviously both aspects will be affected to some extent by the clarity of description and comprehensiveness of the test procedure itself.

Certain generalizations can be made about the likely cause of features in sets of results. Thus a large covariance within a single test in a single laboratory would suggest poor experimental control. The converse of this is, of course, when a laboratory consistently produces the same result for repeat tests with low covariance in the data, even where this is significantly different from the result produced by other laboratories for the same test. That laboratory has good experimental control of its procedure.

Consistent differences between laboratories in otherwise low covariance sets of data suggest some systematic difference in the test procedure being carried out in each laboratory. A consistently large covariance found in the same test by most laboratories suggests a result that is intrinsically sensitive to slight variations in the test procedure. It is, of course, possible to get any combination of the above factors.

The covariance values achieved in this project (see Table 4.4), generally indicate good intra-laboratory control of the test procedures. Thus the average covariance figure for the leaching of zinc from brass, from all the tests that used the standard water, whether at pH 7 or 8.2, was 11.3 %. The corresponding figure for the leaching of lead it was 16.8 %.

The covariance within laboratories was highest where the level of metal contamination was either very high or very low, for example a mean of 22.9 % for the leaching of zinc from galvanized steel where the zinc levels where amongst the highest achieved, and a mean of 65.3 % for the leaching of lead from galvanized steel where the results were close to the detection limit of the analytical methods.

Although the reason for the large scatter when metal levels were very low may be easy to understand, the reason for the same effect at high metal concentrations may be open to more than one explanation. The sensitivity of the solubility of zinc corrosion products to solution pH, combined with the open beaker configuration of the test that allows the loss of CO_2 to the atmosphere, are sources of potential variability in the test procedure used. It has been shown also that devices used in the test to cover the beakers and to hold coupons in the test solution influence the diffusion rate of gases (CO_2 and O_2) from the atmosphere to the test solution and vice versa. The tightness of the system or its permeability to gas may vary from one laboratory to the other, and could explain part of the scatter observed between laboratories.

However, bringing the pH of the test solution to equilibrium with the atmosphere, in the brass tests 3 and 4, or carrying out the test with the standard solution in an enclosed vessel as in brass test 5, did not reduce what was admittedly an already low covariance in the results. A second explanation of large scatter could be the (random) presence of particulate matter (e.g. oxides) which is dissolved by the acidification of the test solution after the sample has been removed at the end of the test.

A third possible explanation of large covariance with high contamination levels is that the metal is still not in equilibrium with the test water at the end of the test period. As this often corresponds to a period of rapid change in the level of contamination, the results may be sensitive to the slight variations that inevitably occur from test to test. Prolonging the test period, or the pre-ageing of samples before carrying out the test procedure, may be a way of reducing this effect.

Another consequence of non-equilibrium behaviour is that a short-term test may only provide a snapshot of the interaction between the alloy and water under test. This may mean that for some metals, the test procedure will discriminate poorly between the effect of different waters on the same alloy, the results obtained being more a reflection of the differences in the speed with which an alloy achieves equilibrium with the waters rather than its long term suitability in those waters.

In the present tests, the variability in the results for both zinc and copper from brass are of little practical consequence, given that the values achieved were so far below the maximum acceptable concentration (MAC) for either element. However, for an element where this is not the case, and where the results indicate that the alloy has not reached final equilibrium with the water, it raises questions as to whether the test period should be extended and how long an element should be allowed to exceed its MAC in a test before the use of the alloy in the test water was deemed unacceptable.

The overall conclusion from the test programme is that each laboratory was achieving sufficient experimental control within a test and that the amount of leaching was not hypersensitive to slight deviations from the protocol. The fact that the laboratories as a group could not consistently achieve means within the same statistical population indicated that they were carrying out slightly different tests. This conclusion implies that agreement between laboratories could be reached if sufficient attention were paid to the procedures being carried out in each one and, as a consequence, if the test protocol were to be specified in even greater detail.

Having demonstrated the principle of a laboratory test, the Conormative Group considered it the task of others to develop a specific test protocol. The question remaining for the current project was to consider to what extent a sit-and-soak test represents the situation in authentic plumbing systems and to what extent any deviation is significant.

The extent to which a simple laboratory test can reflect behaviour in an authentic plumbing system

In order to discuss this question it is necessary to consider the potential mechanisms that can control the leaching of metals in contact with potable waters.

Potential mechanisms controlling the leaching of metals and their implications for a test protocol

1. *Rate of corrosion*: The rate at which a metal corrodes obviously provides the ultimate limit on the rate of contamination of the water that comes into contact with it. The corroded material usually changes its physical form through precipitation and/or changes in its oxidation state, etc. No direct attempt was made to measure the corrosion rate in any of the leaching experiments. Where the corrosion rate is the controlling mechanism, dissolved oxygen levels could be a critical factor. Exposing the coupon in an open beaker, where there is the greatest opportunity for oxygen replenishment, could thus represent the worst case for such a situation.
2. *Level of dissolved oxygen in the test water*: Plumbing systems either have no or only restricted access to the atmosphere. Consequently, where water remains static in such systems for extended periods, it is possible to develop low oxygen concentrations. This can occur most frequently in crevices where bulk exchange of water does not occur and oxygen concentrations are maintained by diffusion only. Reduction in dissolved oxygen concentrations may have a beneficial effect where the contamination level is controlled directly by the rate of corrosion. However, low oxygen levels may also destabilize passivating films or lead to the production of a more soluble lower oxidation state of the metal. In this case, exposure in an open beaker would not be the worst case.

   In test 5 of the conormative experiments, the test pieces were exposed in closed vessels to limit the gaseous exchange with the atmosphere (O_2 and CO_2). This limited the replacement of oxygen and so (to some extent) covered this mechanism.
3. *Galvanic interaction with other metallic components*: Galvanic interaction between materials not only increases the rate of corrosion but, by raising the electrochemical potential at which the metal corrodes, may introduce new effects, for example, the development of passivating films or the conversion of a previously protective ion into an aggressive one.

Attempts have been made in the past to examine galvanic interactions by electrically connecting brass coupons to copper electrodes and then testing the combination in accordance with the conventional BSI procedure. Differences in the results from the uncoupled case were found although, because of practical difficulties in maintaining the integrity of the couple and an increased scatter in the data, it was difficult to decide whether or not the differences were significant.

4. *Solubility of corrosion product*: A deposit is usually produced on a metal's surface in neutral waters, which stifles the corrosion reaction; at the same time the deposit dissolves in the water in contact with that surface. Initially the rate of corrosion exceeds the rate of dissolution and the deposit increases in thickness. This increased thickness reduces the corrosion rate further until the latter equals the rate of dissolution and a dynamic equilibrium is achieved. For this point to be reached, the deposit has to have some combination of effectiveness at stifling the corrosion with sufficient mechanical stability to maintain the thickness of the layer required. When this dynamic equilibrium is achieved, the rate of contamination is then, under defined flow conditions, controlled by the solubility of the corrosion product in the water. The standard sit-and-soak procedure used in this project tacitly assumes that this is the major controlling mechanism.

5. *Mechanical stability of corrosion product layer*: Where the corrosion deposit has insufficient mechanical stability to maintain the thickness required to achieve dynamic equilibrium between the corrosion and dissolution rates, particles of the deposit will break off on an intermittent basis producing peaks of contamination. This type of breakdown would only be expected after prolonged ageing (>70 days for brasses) of the test coupon. Determining the difference between the total metal leached into the test solution and its filtered metal content could give an indication of the presence of this problem.

   A corrosion product that broke down relatively infrequently would produce a peak of contamination in what could otherwise be a generally low background level. This might be difficult to detect if the actual period during which metal concentrations were measured was relatively short. However, the less frequent the occurrence the less important it is if the effect is missed.

   The short term nature of the laboratory sit-and-soak test probably means any effect of this nature will be missed by the current test procedure.

6. *Surface finish of the test coupon*: Various manufacturing processes can change the physical form of the metal's initial surface or produce surface films, either of which may influence the characteristics of the corrosion deposit that is developed when in contact with water. These effects may influence or change the mechanism controlling the level of contamination. The standard sit-and-soak test defines a machined surface that will not be representative of a cast surface, for example. In the first set of conormative tests, actual galvanized steel pipe was used to overcome precisely this sort of problem.

7. *Ageing*: Time is required for the film on a metal surface to develop fully. Until this happens, the long term potential of a metal to contaminate the supply will be uncertain. An even more critical effect of ageing is to change the ratio of the elements at the surface of the uncorroded metal. This may result in a delay (induction period) in the contamination of the water by certain of the metal's trace constituents until they have been sufficiently concentrated at the surface.

   The standard sit-and-soak test is, of course, very short. However, if long term ageing was thought to be potentially a significant factor, samples could be preconditioned for whatever length of time was considered appropriate. The conditions could be chosen for practical convenience rather than bearing any particular relation to the final test protocol. Thus, all 20 coupons could be suspended in a 5-litre beaker with the test water flowing through.

8. *Effect of flow regime experienced*: The speed with which a metal's surface comes to equilibrium with a water, and in some cases the characteristics of the corrosion product which is developed, can depend on the flow regime that it has experienced. At present, the standard sit-and-soak test defines static conditions. However, if this mechanism was thought potentially to be significant, different flow regimes could be incorporated into an ageing procedure to cover this.

9. *Aggressivity of the test water*: Different metals, and even different phases of the same alloy, have different vulnerabilities to particular water compositions. The original BSI test water was chosen for its aggressiveness towards lead rich phases. However, it has low aggressiveness to metals that form passivating films, e.g. stainless steel, aluminium, etc.

   In the current project, sit-and-soak tests were carried out using a range of waters. This could be made the standard procedure when testing a metal for general acceptability. The control mechanisms covered by the sit-and-soak test used in this project, and its potential for adaptation, are summarized in Table 4.12.

Table 4.12 Control mechanisms and the sit-and-soak test

Control mechanism	Comments
Solubility	Covered by the current sit-and-soak test
Galvanic interaction	Not covered by the current sit-and-soak test but galvanic test couples have been used in the past
Dissolved oxygen levels	Not covered by current protocol but tests could be carried out in enclosed vessels to (partially) meet this requirement
Surface finish of metal	Not covered by current sit-and-soak test but the difficulty has been met before by using manufactured pipe sections as test pieces; may be practically more difficult with fittings
Ageing	Not covered by current sit-and-soak test but could readily be met by a sample preconditioning stage
Water composition effects	Not covered by current sit-and-soak test but other test waters could and have been used

Pipe-rig results

The main advantage of using a rig procedure is that operating conditions may simulate as closely as possible the authentic situation. Consequently, the mechanism controlling corrosion and water contamination is built into the test apparatus without having to be identified. Disadvantages are the expense, the time involved and the large volume of water needed, which practically implies the use of tap water.

Main outcomes of rig experiments are:

(i) Three distinct behaviours can be identified in the evolution of the level of contamination during the course of the test run:

- Exponential decrease to a minimum value;
- Increase to a maximum value that then either remains constant or which decreases slightly;
- Peak contamination after an initial period of low values (during several weeks or months) followed by a gradual decrease.

  The shape of the curve depends on the material tested and can be different for different metals in an alloy. For a given metal (e.g. copper from copper pipe), the shape can also be different with different test waters and even, for a given test water (e.g. TZW concentrate with copper pipe), it can be different at different stagnation times. Time to reach equilibrium and contamination level also depends on test water characteristics.

(ii) Variations in the characteristics of test water can influence the contamination level. This has been shown for pH and temperature but could be expected also with other parameters (oxygen, alkalinity, sulfate, etc.) if significant variations occur during test operation. Tap water is usually subject to random or seasonal variations (mainly with surface water). Water analyses are then necessary in parallel with metal analyses to avoid misinterpretation of contamination results.

(iii) Tests on pipe rigs with brass fittings show that there is possible influence of the fitting material on the behaviour of the pipe material (reduced contamination by copper due to zinc migration from brass). More generally, this would mean that a material should be tested in authentic situation (fittings with the material(s) they are designed for).

(iv) The use of local tap waters in pipe-rig experiments did not allow the reproducibility of the results between laboratories to be assessed. Slight differences in the test device or test operation could, as for sit-and-soak tests, affect test reproducibility. An accurate definition of test device and test conditions is necessary to reduce this risk. Nevertheless pipe-rig reproducibility will have to be assessed.

Reproducibility within each laboratory can be assessed by comparing copper concentrations from copper rigs and from copper rigs with brass fittings. For all laboratories, copper concentration curves overlap almost perfectly after the initial period where migration of zinc from brass fitting influence (reduce) the migration of copper.

Information from reference rigs is more complete and closer to reality than is information given by a simple sit-and-soak test where only 24-hour stagnation samples are analysed over a short period of time (2 weeks). However, adaptations of sit-and-soak tests could be considered as getting more information on different possible mechanisms (Table 4.13) or to produce stagnation curves. However, static tests cannot cover the influence of flow conditions, which appear also to be an important factor in authentic situations.

Table 4.13 Comparison of the advantages and disadvantages of a sit-and-soak test versus rig tests

Sit-and-soak test		Rig test	
Advantages	Disadvantages	Advantages	Disadvantages
Cheap			Expensive
Short time scale	Does not cover ageing effects	Covers ageing effects	Long time scale
Generally good control of experimental conditions	Experimental conditions may not be authentic and introduce a different control mechanism	Relatively authentic exposure conditions	Poor control of exposure conditions may give problems of reproducibility
Good control of surface finish of coupon	Surface finish may not reflect reality	Authentic surface condition	Poor control of surface finish may introduce variability in the answer
Surface/area volume ratio well controlled	Surface/area volume ratio may not reflect reality	Surface/area volume ratio reflects reality (for a given pipe diameter)	Surface/area volume ratio not well controlled
Small volume of test water required (synthetic or tap water of controlled quality can be used)			Large volume of water required, really has to be on the tap (variation in water quality may introduce scattering of the results)

4.2.5 Conclusions

Because of the variety and specificity of the mechanisms controlling the interaction between water and metallic materials, and as the test water is itself a significant factor in determining the leaching from metals, the procedures used to assess organic materials are not valid for testing metallic materials.

The variety of situations that can occur in authentic plumbing systems cannot be fully represented by any single simple sit-and-soak or pipe-rig test procedure.

The pipe-rig test procedure, carried out in this research can provide the information necessary for the evaluation of potential migration from metallic materials when in contact with potable water.

Conclusions regarding sit-and-soak tests

Experiments carried out with sit-and-soak tests show that it is possible to get reproducible results within laboratories. However, the test has proved to be very sensitive to slight variations in procedure. Further development and improvements in the definition of the procedure will be necessary to achieve reliable inter-laboratory reproducibility.

The sit-and-soak test procedure used in this study, adapted from that in BS 7766, tacitly assumes that the migration of metals in water is governed by the solubility of corrosion products. However, adaptations of the procedure could be possible to cover many of the other potentially controlling mechanisms.

A simple sit-and-soak test procedure (or a set of such tests) can be useful in identifying which controlling mechanisms are operating in a particular situation. However, there appears to be no ready way of correlating the results of such static tests with those contamination levels expected in authentic situations. Consequently sit-and-soak test procedures cannot be reliably used to produce an absolute evaluation of the potential migration from any particular metal.

Conclusions regarding rig tests

A pipe-rig test procedure can simulate an authentic situation and so give a direct quantitative assessment of the potential to contaminate by metals in relation to the particular operating conditions and test water used. Consequently pipe rigs are necessary for the evaluation of potential migrations from metallic materials.

The operating conditions for pipe rigs need to be standardized and their inter-laboratory reproducibility assessed.

The selection of test water(s) is not within the scope of the test protocol itself but should be within the scope of regulation. The research shows that it is not possible to use a single water for all materials to be tested. Test water quality might be chosen according to the material or category of material to be tested, or a range of water qualities might be selected to cover all situations.

The experiments with pipe rigs have shown that pipe fittings can influence the migration of metals from the pipe with which they are used (compare the results from copper rigs with those from copper rigs with brass fittings). The consequence of this is that it is necessary to test the material used to make fittings in authentic situations, that is, connected with the pipe materials for which they are designed.

A comparison of copper concentrations after half-an-hour stagnation in copper rig experiments at CRECEP with field data observed in Paris shows a good agreement in the level of concentrations. Such comparisons would need to be developed in other situations to assess the actual 'representativity' of pipe-rig experiments.

4.3 TEST PROCEDURE FOR CEMENTITIOUS MATERIALS

4.3.1 Introduction

A cement can be defined as a substance that sets and hardens due to chemical reactions that occur upon mixing with water. Cement based materials include two general components:

- the aggregates – these constitute the basic structure of the material, for example sand in the case of cement–mortar lining, sand and gravel in the case of reinforced concrete pipes;
- the binder – responsible for the cohesion and mechanical properties of the material.

Figure 4.15 shows the basic structure of cement-based materials, exemplified by a cement–mortar lining. The binder consists of hydrated cement produced by reacting water with anhydrous cement, which contains calcium silicates and calcium aluminates in various proportions.

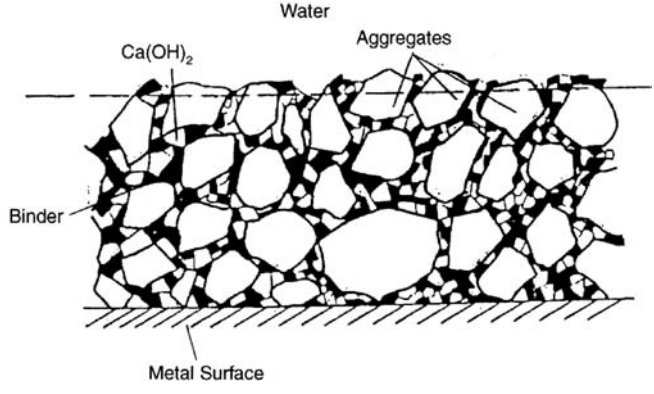


Figure 4.15 Schematic structure of cement-based material

Table 4.14 Typical compositions for some type of cements used for manufacturing pipe)

Parameter	Portland cement	Blast furnace cement	Calcium-aluminate cement
SiO_2 (%)	21	27	3.5
CaO (%)	65	48	38
Free CaO (%)	1.5	0.5	0.5
$A1_2O_3$ (%)	5	13	36
Fe_2O_3 (%)	2.5	1.5	18
SO_3 (%)	2.5	3.8	0.1
Na_2O (%)	0.3	0.4	0.1
K_2O (%)	0.8	0.8	0.05
MgO (%)	2.0	2.8	0.4
Density (g/cm^3)	3.1	2.9	3.2
Specific surface (cm^2/g)	3870	3850–8450	2750

The basic constituent, the clinker, is obtained from the pyroprocessing of calcareous and argillaceous rock. Portland types of cement include those that are mixtures of clinker and pozzolana, blast furnace slag and fly ash, in a range of combinations. In addition, non-Portland calcium aluminate cements (formerly called high alumina cement or HAC) are manufactured by pyroprocessing bauxite and lime.

Generally, concrete used for water treatment plant pipes, water tanks, and filters is made using (ordinary) Portland cement, whereas cement–mortar linings can be made of different types of cements, such as Portland cements, blast furnace cement or the non-Portland calcium aluminate cement. Each type of cement has a typical composition. Table 4.14 gives the typical composition of the primary cements used for manufacturing pipe.

Structure of the cement matrix in concrete and mortar

During manufacturing of cement-based pipeline products, the silicates and aluminates present in the cement react with water to form products of hydration and, in time, these set to a hard mass. The various solid phases formed come into thermodynamic equilibrium with the interstitial water (pore water), which is rich in calcium, sodium, and potassium hydroxide phases. The presence of these hydroxides raises the pH of the pore water solution to about 13 or 13.5. Table 4.15 gives typical compositions of pore solution for two types of cement: Portland and blast furnace slag cement.

Carbonation of cement based materials in contact with water

Contact of cement based materials with water produces changes in the cement matrix and in the water composition. The interactions between the cement material and

Table 4.15 Typical composition of the pore solution for two types of cement

Parameter	Portland	Blast furnace
pH	13.4	13.2
Calcium (mg Ca/l)	65	37
Magnesium (mg Mg/l)	0.25	0.30
Sodium (mg Na/l)	2 200	1 600
Potassium (mg K/l)	11 500	8 500
Aluminium (mg Al/l)	4.5	25
Sulfate (mg SO_4/l)	550	160
Silica (mg SiO_2/l)	12	32

the water result from the great surface area of contact between these two phases, especially in the pores. The ions present in the pore water (such as OH^-, Ca^{2+}, Na^+ and K^+) tend to escape into the transported water, which normally contains smaller concentrations of these constituents.

On the other hand, the ions present in the transported water, such as aqueous carbon dioxide and bicarbonate ion, tend to enter into the pore water. The reaction between the hydroxide ions from the pore water and the dissolved aqueous carbon dioxide and bicarbonate ion forms carbonate ion (CO_3^{2-}). As a result, conditions suitable for spontaneous calcium carbonate precipitation may exist in the pores, near the exposed surface. This process is called carbonation. These calcium carbonate deposits can reduce the interaction between transported water and the chemical species in the pores.

Blockage of the pores by carbonation will not occur if a significant proportion of the calcium ions from the calcium hydroxide leaches into the transported water, because the solubility product for calcium carbonate will not be sufficiently exceeded. Then the calcium ions present in the transported water will not contribute to the formation of interstitial calcium carbonate deposits and, consequently, the transported water gains calcium ions. Carbonation can be induced by bringing CO_3^{2-} ions to the pores by dry pretreatment with gaseous CO_2 or a wet pretreatment with water containing a sufficient HCO_3^- concentration. CO_2 and HCO_3^- are converted to CO_3^{2-} in the pores of the material because of the high pH value according to the following reactions:

$$\text{Dry pretreatment: } CO_2 + Ca^{2+} + 2OH^- \Rightarrow CaCO_3(s) + H_2O$$
$$\text{Wet pretreatment: } HCO_3^- + Ca^{2+} + OH^- \Rightarrow CaCO_3(s) + H_2O$$

Influence of water composition

In a calcium carbonate aggressive water, dissolution of the locally precipitated $CaCO_3$ proceeds continuously into the cement based material. The alkaline properties of the cement are inadequate to neutralize the $CaCO_3$-dissolving properties of the water.

If the water in contact with cement is in equilibrium or is oversaturated with respect to calcium carbonate, its deposition leads to blocking of the pores. The calcium carbonate deposit is then stable and the cement material is protected for as long as the transported water remains under these conditions. If the transported water has a low total inorganic carbon (TIC), the deposit may not lead to blocking of the pores, regardless of whether the water transported is oversaturated with $CaCO_3$ or not. In this case the amount of $CaCO_3$ precipitation possible is smaller than the amount of calcium species dissolved.

Effects of cement-based materials on water quality

Contact between water and cement materials can lead to lime (calcium) leaching, which induces a substantial pH increase in the drinking water. The effect on water quality can be seen as:

- an increase in pH. Depending on the buffer capacity of the water, it can be that the pH value rises above the limit value of 9.5. The pH may be as high a 11 to 12 in 'worst-case' conditions (Conroy and Oliphant, 1991);
- an increase in the aluminium content of the drinking water (Conroy and Oliphant, 1991). The different cement types contain different aluminium contents. Some aluminium goes into solution because of the high pH value of the water caused by lime leaching;
- an increase in the potassium content of the drinking water. This is an indicator of a leaching process;
- an increase in hardness of the water.

One of the objectives of the test is to investigate the leaching of mineral micropollutants, such as heavy metals, from cement-based materials. All cements, irrespective of their type, contain small but variable amounts of a range of heavy metals derived from their constituents. These are generally present at trace level.

The behaviour of heavy metals in hydrated cement matrices is not entirely clear. Much research, however, tends to indicate that they are essentially immobilized as insoluble hydroxides within the structure of the hydration products. On the other hand, it is conceivable that under some conditions, they might be 'solved' and transported to the surface through the pore system. The level of increase in the pH of a water and the amount of leaching of other elements which takes place, depends on:

- the TIC and buffer capacity of the transported water;
- the type of cement;
- the contact time between the water and the cement material;
- the pipe diameter.

4.3.2 Technical Background

Preconditioning of test samples

The nature of cement based materials begins to change as soon as they are manufactured and this continuing change cannot easily be controlled or predicted as it is affected by for instance, storage conditions and time of storage. After pipe manufacturing, during storage and transportation, the natural carbonation process takes place and transforms the surface of the mortar lining by $CaCO_3$ deposition into the pores. Also pipes commonly undergo some form of preparation, such as hydraulic tests, disinfecting or rinsing, before they are brought into service. This can lead to changes in the nature of the material. Therefore, in testing cement-based materials, a preconditioning stage may be necessary in order to give each material arriving from the factory a comparable state of carbonation or maturity, including being able to simulate the effects of preparation prior to intended use.

Preconditioning can be a particularly important step in that the validity and reproducibility of the migration test itself might directly depend on the preparation of the test samples.

In the conormative research project, preconditioning with liquid and gaseous carbonation of the cement materials was tested. The preconditioning consists of wet contact with several water types (soft and moderate hardness) or dry contact with CO_2 under several conditions (CO_2-pressure, time). The effect of preconditioning is compared with unpreconditioned cement mortar specimens.

The effect and the results of preconditioning have to be assessed against the following questions:

- Does preconditioning mask/minimize the effects of different ageing times or storage conditions?
- Does preconditioning improve intra- and inter-laboratory reproducibility (with respect to indicative parameters such as pH, aluminium, calcium, potassium, etc.)?
- Does preconditioning improve the relationship with practice?
- Is preconditioning required in order to avoid interference of hydroxyl ions with other parameters to be measured (e.g. taste, aluminium, organic and mineral micropollutants, etc)?

Migration tests

The objective of the research into the migration test was to assess the influence of water characteristics (mainly pH, calcium carbonate aggressiveness and mineral content) on the migration of micropollutants and on the organoleptic quality of water.

The influence of water characteristics on the behaviour of cement-based materials tends to be very significant. Although the dissolution of lime depends on water pH,

it is dependent to a greater extent on other factors such as the aggressiveness and mineral content of the water. Some metallic elements or other substances may be leached with aggressive water of low mineral content, while leaching will tend to be reduced in non-aggressive water of medium mineral content.

The test protocol will be the same as the protocol described in the European draft standard of CEN TC164/WG3 for organic materials: test samples (pipes segments) will be filled up with test water for three successive 72-hour periods. The effect of varying the test water characteristics has to be assessed against the following criteria:

- sensitivity of the test method with respect to potential micropollutant leaching;
- reproducibility of test results between and within laboratories (with respect to pH, aluminium, calcium and potassium);
- practicability of water preparation and control;
- migration water should be representative of natural drinking waters or yield representative data, with respect to pH, $CaCO_3$ content (hardness and alkalinity), aggressiveness, silica content and occurrence in different countries.

4.3.3 Effect of Preconditioning and Migration Water

Experimental procedure

The full experimental procedure is summarized below. This full procedure has been applied only for the first mortar tested (ordinary Portland cement). Results from this first set of experiments have allowed some experimental conditions for further tests with blast furnace cement (BFC) and high alumina cement (HAC) mortars to be deleted (see page 165).

Preconditioning: Two categories of method have been used for the preconditioning of cement based materials:

- liquid contact ('wet process'): pipe segments are filled up with the preconditioning water;
- gas contact ('dry process'): pipe segments are filled up with carbon dioxide at a given pressure.

On the basis of existing data, the following different preconditioning conditions were defined:

Reference: no preconditioning. Samples should be stored in the lab until the beginning of migration tests.

Gas contact, CO_2 pressure and exposure duration are as follows: D1: 1 bar CO_2 during 5 days; D2: 2 bar CO_2 during 5 days; D3: 1 bar CO_2 during 1 day; D4: 2 bar CO_2 during 1 day.

Before applying CO_2, samples should be filled up with deionized water for half an hour in order to moisten the cement surface and to allow further carbonation by gas.

Liquid contact, four preconditioning waters should be used with characteristics as follows:

(1) *Wp1*: 20 mg/l $CaCO_3$ of alkalinity and calcium hardness at pH = 7.0.

(2) *Wp2*: 200 mg/l $CaCO_3$ of alkalinity and calcium hardness, at equilibrium (pH ≈ 7.4);

(3) *Wp3*: Same as Wp2 + 0.25 mmole / l CO_2 (pH ≈ 7.2),

(4) *Wp4*: Same as Wp2 + 1.0 mmole / l CO_2 (pH ≈ 6.8).

Synthetic waters should be prepared by dissolving calcium chloride and sodium bicarbonate in deionized water and adjusting the pH by bubbling CO_2 and air.

For liquid contact preconditioning, pipe segments should be filled up with water for successive 24-hour periods (72 hours during the weekend).

The initial and minimum preconditioning step consists of five successive contact periods; three times at 24 hours, once at 72 hours and once at 24 hours.

At the end of this procedure, if the pH is below 9.2, migration tests can start. If not, then the same procedure should be applied one more time. At the end of the second week, migration tests should be performed whatever the pH value.

CRECEP, WRC and Kiwa have performed experiments with liquid preconditioning. Kiwa, LHRSP and TZW have performed experiments with gaseous preconditioning. Reference, unpreconditioned, samples have been tested in the five laboratories.

Migration tests: Six test waters have been used with approximately the following characteristics:

Wm1: 200 mg/l of alkalinity and Ca hardness at equilibrium (pH ≈ 7.4);

Wm2: same as Wm1 + 0.25 mmol/l CO_2 (pH ≈ 7.2);

Wm3: same as Wm 1 + 1.0 mmol/l CO_2 (pH ≈ 6.8);

Wm4: 20 mg/l of alkalinity and Ca hardness at equilibrium (pH ≈ 8.2);

Wm5: same as Wm4 + 0.25 mmol/l CO_2 (pH ≈ 6.6);

Wm6: same as Wm4 + 1.0 mmol/l CO_2 (pH ≈ 6.0).

For the first trials, two laboratories (LHRSP and CRECEP) used natural mineral waters (Evian and Volvic) modified by adding hydrochloric acid to reduce alkalinity to 200 and 20 mg/l $CaCO_3$ approximately. The three other labs (Kiwa, TZW and WRC) used synthetic waters prepared by dissolving calcium chloride and sodium bicarbonate in deionized water.

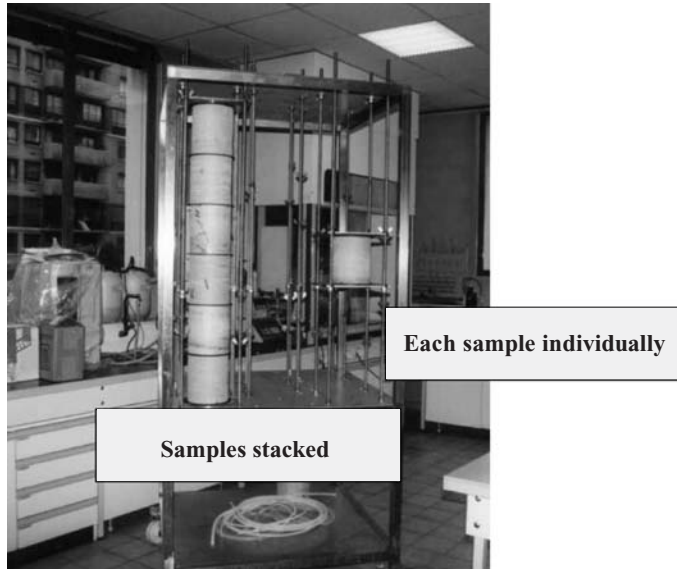


Figure 4.16 Device for preconditioning and migration tests

Test device. For preconditioning, six pipe segments have to be treated with the same water. To ensure good reproducibility, the six pipe segments were stacked in a column to be treated under the same conditions (Figure 4.16). For migration tests, each pipe segment was treated individually (Figure 4.17).

The test devices used are slightly different for each of the five laboratories, but the pipe segments are always set between two stainless steel plates with PTFE gaskets for tightness (Figure 4.17).

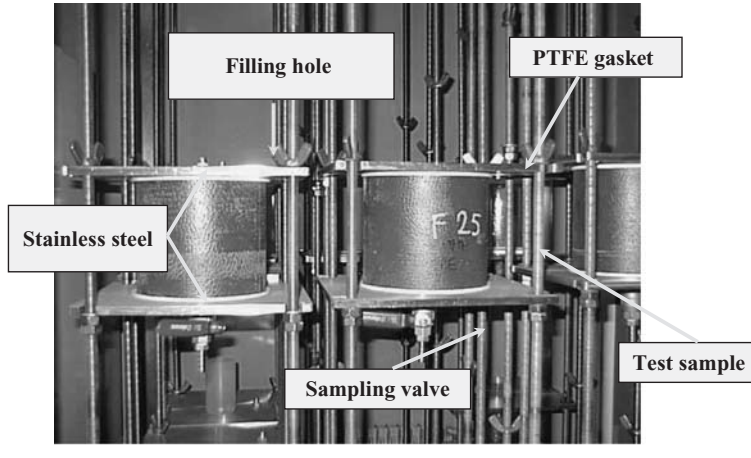


Figure 4.17 Example of device for migration tests

All materials used for the device should be tested to check that they do not contaminate water. A procedural blank in the form of a glass cylinder should be tested in parallel.

Dimension of pipe segments. Samples of materials are taken from actual pipes provided by the manufacturers. Thus the surface/volume ratio (S/V) is fixed by the diameter of the pipe sample. For practical reasons it is easier to handle small samples. Consequently, pipe segments of 150 mm length and 150 mm diameter were used ($S/V = 260\ cm^2/l$). These dimensions allow sufficient cement lining surface and a sufficient volume of water for analysis. Samples were cut in the factory and delivered to each of the five laboratories in the finished form, ready for tests.

Analytical determinations

During preconditioning. pH, aluminium concentration and, optionally, conductivity were determined after each 24- or 72-hour contact period during wet preconditioning. Only CO_2 pressure was controlled and adjusted during dry preconditioning.

During migrations (3×72 hours). pH, aluminium concentration and, conductivity were determined after the first and second migration periods. At the end of the third 72-hour period, test waters were sampled for analysis of the following parameters:

pH; total organic carbon;

organoleptic and aesthetic parameters (turbidity, flavour);

mineralization (conductivity, alkalinity, calcium, magnesium, sodium, potassium, chloride, sulphate, nitrate);

mineral micropollutants (aluminium, iron (to check corrosion of cast iron if necessary), chromium and lead).

Materials tested Three materials were tested:

- Ordinary Portland cement (OPC) factory applied using the TATE process (December 1995);
- Blast furnace cement (BFC) factory applied by spinning (July 1996);
- High alumina cement (HAC) factory applied by spinning (April/May 1997)

These materials were chosen because they are representative of what is used in the pipe industry and because they have different compositions:

- Portland cements are calcium-silicate based materials, with less than 2 % free lime;
- Blast furnace cements are mixes of about 30 % OPC and 70 % slag.
- High alumina cements are calcium-aluminate based materials, without free lime.

Tested samples were ductile iron pipe with cement mortar lining, of 150 mm internal diameter.

The full procedure, as described above, was applied for OPC (nine preconditioning conditions and six test waters). After experiments with OPC, some experimental conditions were deleted for tests with HAC and BFC as they did not appear to give additional information. There were dry preconditioning with 1 bar CO_2 (D3 and D4); wet preconditioning with medium mineralized water with added CO_2 (Wp3 and Wp4); and migration waters with 0.25 mmole/l CO_2 (Wm2 and Wm5).

Experimental results

First examination of experimental results has shown that some parameters are good indicators of the behaviour of the materials in contact with water for the purpose of the research: pH, aluminium, calcium and potassium. The evolution of these elements is strongly influenced by the material and by test conditions (preconditioning and test water). Lead and chromium have never been detected at significant levels in any of the experiments carried out for the three materials.

Effect of preconditioning Liquid preconditioning. With a soft (low mineralized) preconditioning water, pH is high (>11 for OPC and BFC) and does not decrease significantly with contact time. At the end of preconditioning, pH was still above 9, even if preconditioning was prolonged for another week (3×24 h, 72 h, 24 h). With medium mineralized water, pH was lower (<9 for BFC and HAC) or decreased rapidly below 9 (OPC).

In the first case (soft water) there was no carbonation of the cement, but probably the opposite, an opening of the pores. In the second case, there was effective carbonation ($CaCO_3$ deposit) of the surface, which reduces lime migration in water.

With a soft preconditioning water, the scattering of pH results between the three laboratories seemed to increase with contact time (BFC and HAC), whereas there is good agreement between them for pH and aluminium with medium mineralized water. Aluminium concentration levels were very different for the three materials (HAC $>$ OPC $>$ BFC) but were always in relation to the pH for the individual material.

Effect of preconditioning on migration results. The effects of preconditioning and of migration test water were investigated using multifactor ANOVA (analysis of variance). This statistical tool breaks the variability of data (pH, Al, Ca or K) into contributions due to various factors (preconditioning conditions and CO_2 added in test water).

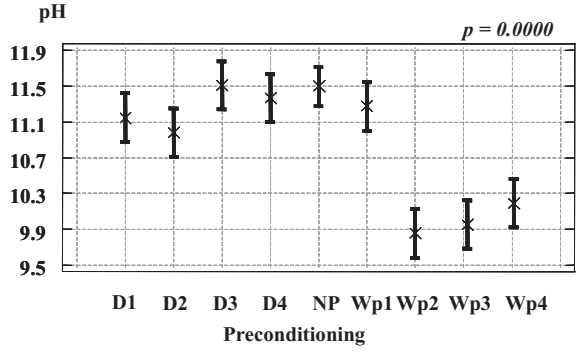
The analysis showed whether one or both (or neither) factors had a significant effect on the variability and which level of the factor is different from which other. The p value indicates whether the factor has a significant effect on the variability ($p < 0.05$) or not ($p > 0.05$).

Only data obtained with synthetic waters have been considered in these statistics as it appeared that the origin of water (natural or synthetic) had a major effect on the results, in particular for aluminium.

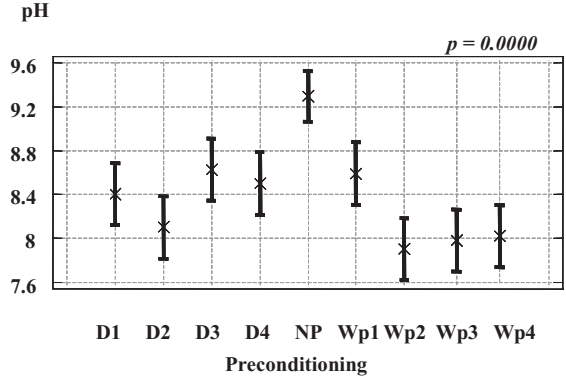
Ordinary Portland Cement. The effect of preconditioning is significant for the four parameters tested (pH, Al, Ca and K) for soft migration waters and for three parameters (pH, Ca and K) with medium mineralized migration waters. All preconditioning, except Wp1 (soft water pH 7) significantly reduced aluminium in soft migration water, but only wet preconditioning using a medium mineralized water (Wp2, Wp3 and Wp4) reduced pH in soft migration water.

All preconditioning significantly reduced pH in medium mineralized migration water with a better efficiency for Wp2, Wp3 and Wp4 (medium mineralized preconditioning water), followed by D1 and D2 (dry preconditioning, 5 days).

Figure 4.18 illustrates the effect of preconditioning on pH.



(a)



(b)

Figure 4.18 Least square means and 95 % confidence intervals, by preconditioning, for pH after migration using low mineralized water (a) and medium mineralized water (b) for ordinary Portland cement

Calcium migration was increased by Wp1 (soft water preconditioning) for soft migration test water.

For medium mineralized migration water, there was no migration of calcium from the material but, on the contrary, calcium precipitates on the material (initial calcium concentration in migration water is 80 mg/l).

The results for potassium show that the mechanism is different than for other parameters. In fact potassium leaching was decreased in all cases by wet preconditioning. These results indicate that potassium is leached from the cement in contact with water whatever the water characteristics are. The same potassium concentrations were observed with soft and medium mineralized migration waters. (Note that potassium leaching will tend to increase the pH as it is leached from the cement as KOH).

Differences also appeared between preconditioning waters Wp2, Wp3 and Wp4 (medium mineralized water with 0, 0.25 and 1 mmole/l CO_2 added); Wp2 (water at equilibrium) always being the most 'effective' (i.e. differences with unpreconditioned samples are greater). Wp3 and Wp4 were deleted from the following experiments. For dry preconditioning also, differences appear between D1 and D2 (5 days, 1 and 2 bar) and D3 and D4 (1 day, 1 and 2 bar). D3 and D4 were deleted from the following experiments.

Blast Furnace Cement. The effect of preconditioning is significant for pH and aluminium for soft migration water but only for potassium is the case of medium mineralized migration water. However, some effects can be observed for other parameters but they are not statistically significant. General trends are almost identical to OPC, except for pH in soft migration water. In fact, the pH increase was lower with dry preconditioned samples than with wet preconditioned (Wp2).

We can also observe that the material was less reactive than OPC: lower pH, aluminium and potassium concentrations, no significant change of calcium concentration in medium mineralized migration water (initial Ca = 80 mg/l).

High Alumina Cement. No significant effect of preconditioning was detected for the four parameters tested in either migration test water even if some difference appears in the graphs, which indicates the same general trends as for the other materials. pH levels were much lower with this material than with OPC and BFC but aluminium leaching was much more important especially in soft migration water (3 to 8 mg Al /l).

Further experiments however (see Section 4.3.4) show very clearly that preconditioning does in fact have an important and very significant effect. The effect of preconditioning can be 'masked' by the effect of migration test water characteristics (free CO_2 added) which is very important in the case of high alumina cement.

Effect of migration test water characteristics Initially, two main characteristics were expected to have a major influence on reactions of cement-based materials in contact with drinking water, namely the alkalinity of the water (carbonate and hydrogen carbonate contents) and the 'aggressivness' of the water (free CO_2 content).

(the arithmetical sum of alkalinity and free CO_2 contents gives the total inorganic carbon, TIC, of the water).

In fact inorganic carbon contained in water can react with the material to form calcium carbonate ($CaCO_3$) on the surface of the material (carbonation), thus closing the pores of the cement matrix. If TIC is not sufficient for that, no carbonation of the surface occurs and migration of some elements (Ca, K) continues or may be increased. Also if the water is aggressive to calcium carbonate, the deposit is not stabilized and continued migration from the material occurs.

Actually the results from the research confirm these expectations but the origin of the test water (natural or synthetic) also has a very important effect on aluminium migration. This effect has been explained by the presence of silica in natural water (see below).

Effect of test water alkalinity. The effect of alkalinity appears obvious for all materials when comparing results for soft migration water (20 ppm $CaCO_3$) and medium mineralized migration water (200 ppm $CaCO_3$). pH increase and aluminium leaching were far more significant with soft water than with medium mineralized water. Calcium concentration always increased (calcium migration from the cement) in soft waters (initial Ca = 8 mg/l) but it decreased or remained unchanged in medium mineralized water (precipitation of $CaCO_3$ or equilibrium).

On the other hand, potassium leaching is not affected by water alkalinity. Final potassium concentration seems to depend mainly on the contact time (it decreases with time in successive contact periods).

Effect of free CO_2 content of test water (aggressiveness). The effects observed were similar for all materials but are more apparent for high alumina cement. Again, no significant effects were observed on potassium leaching. Looking at pH and aluminium concentration it is seen that final values are lower when test waters (soft or medium mineralized) contain more free CO_2 (more 'aggressive' waters). However, starting pHs were also lower in that case and aluminium concentration depends greatly on pH.

When looking at calcium concentrations the effect of water aggressivness is observed as follows:

- in soft water: calcium leaching is higher with aggressive water (1 mmole/l CO_2);
- in medium mineralized water: calcium concentration decreases (below 80 mg/l) with water at equilibrium, indicating $CaCO_3$ precipitation. It decreases less (OPC), remains stable or sometimes increases (BFC, HAC) with aggressive waters.

It must be noted also that CO_2 addition into test water makes the water less stable (CO_2 tends to escape in contact with atmosphere). Using such water may increase scattering of results.

Comparison of natural and synthetic migration waters, effect of silica. First results obtained with OPC have shown important differences in aluminium concentrations in the results obtained by CRECEP and LHRSP on the one hand, Kiwa, TZW and

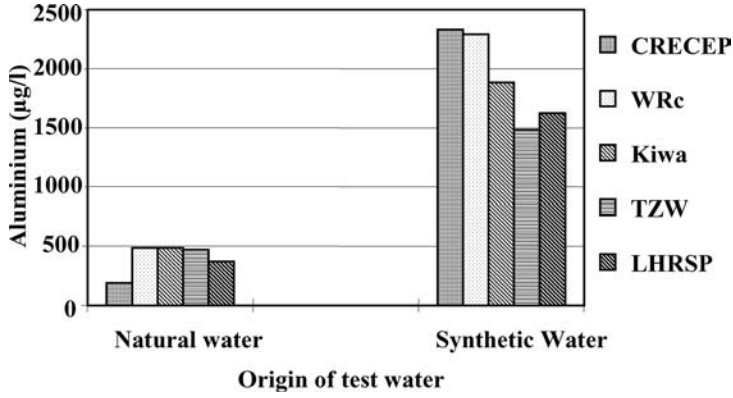


Figure 4.19 Comparison of aluminium concentrations in natural and synthetic, low mineralized migration waters. Results after the third migration, for five laboratories, without preconditioning

WRc on the other. Complementary experiments have been carried out to find out where these differences were coming from (test procedure, laboratories analytical capabilities, test water, etc.).

CRECEP and LHRSP used natural waters because they are more convenient for taste evaluation. Alkalinity of natural waters has been corrected to obtain 20 ppm and 200 ppm $CaCO_3$. The differences were always significant and very large with soft waters, but differences also appeared with medium mineralized waters. Aluminium leaching is lower in natural waters than in synthetic waters.

All laboratories performed experiments on OPC with natural and synthetic waters to ensure that the differences were due to the origin of water. Figure 4.19 shows this actually to be the case, but also that pH is not affected by the origin of the water. The origin of the differences proved to be the silica concentration of natural waters (28.5 mg SiO_2/l in soft water, 13.6 mg SiO_2/l in medium mineralized water).

4.3.4 Reproducibility Tests

In experiments described previously for the three materials, only one sample was tested in each laboratory for each test condition (preconditioning + migration test water). Five replicates in five different laboratories were available for non preconditioned samples and only three replicates for preconditioned samples. Results from the experiments showed that the same tendencies were observed in all laboratories and were generally consistent. However, some differences were also observed and it is difficult to draw conclusions about the reproducibility and repeatability of the test between and within laboratories. To fill this gap, complementary experiments were carried out as described below.

Table 4.16 Characteristics of waters used for experiments

	Preconditioning water	Migration test water
pH	7.4	8.2
Hardness (mg CaCO3/l)	200	20
Alkalinity (mg CaCO3/l)	200	20
Calcium (mg Ca/l)	80	8
Chloride (mg Cl /l)	142	14.2
Sodium (mg Na/l)	92	9.2
Bicarbonates (mg HCO_3/l)	244	24.4

Test procedure

Experiments were performed on HAC mortar samples (applied by spinning on cast iron) in September 1997. Spare samples of the material tested in April/ May 1997 were used for this purpose.

Tests were carried out without preconditioning and with liquid preconditioning in medium mineralized water. Low mineralized synthetic water was used for migration (3×72 hours) in all laboratories. Characteristics of preconditioning and migration test waters are given in Table 4.16.

For both test conditions (with and without preconditioning), each laboratory performed the test on five replicates (at the same time).

Conclusions

Between laboratory reproducibility: All labs observed the same tendencies for all parameters with or without preconditioning. Significant divergences remain between laboratories for most of the parameters tested, and reproducibility was improved by preconditioning.

Within laboratories repeatability: All laboratories obtained comparable repeatability for each parameter, and coefficients of variation were low (<10 %) for pH, conductivity and Na. They were higher for Al (20–30 %) Ca (10–20 %) and K (20–50 %). Repeatability was improved or unchanged, depending on the parameter, with preconditioning.

4.3.5 Effect of Preconditioning at Different Ageing Times

One important question about preconditioning is: does it mask / minimize the effects of different ageing times or conditions?

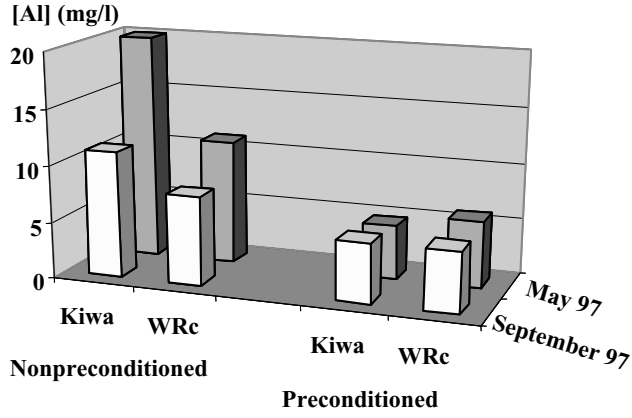


Figure 4.20 Comparison of aluminium concentrations after the third migration in May and September 1997, with and without preconditioning

Figure 4.20 shows aluminium concentrations after the third migration period for the same material (HAC) tested in two laboratories in May 1997 and September 1997 with the same test conditions: liquid preconditioning with medium mineralised water; and low mineralized synthetic migration water at pH 8.

Aluminium concentrations in non-preconditioned samples appeared to be lower in September than in May, and the scattering of results between laboratories was also very important with greater differences in May. For preconditioned samples, differences between the two dates and scattering between laboratories were much lower and all results were in the same range.

These results tend to demonstrate that preconditioning is effective and necessary to minimize the effect of natural uncontrolled ageing, and that liquid preconditioning with medium mineralized water is an efficient means for doing so.

4.3.6 Conclusions

Preconditioning

Preconditioning has a significant effect on the migration behaviour of the material in contact with water. Liquid preconditioning with medium mineralized water and gaseous preconditioning decrease exchanges between the material and water by stabilizing the material.

Liquid preconditioning with low mineralized water increases the exchange between the material and water, and also the range of pH and aluminium concentrations increases during preconditioning. There is no stabilization of the material with such preconditioning water.

Gaseous preconditioning appears to be less practicable and also less representative of the service condition than is liquid preconditioning.

Liquid preconditioning with medium mineralized water at equilibrium proved to be efficient for two important reasons: it improves test reproducibility; and it minimizes the effect of ageing time of the material.

Migration test water

Three parameters; alkalinity, free CO_2 (aggressivity) and silica, were found to have a major influence on the test results:

Soft water was more aggressive to cement-based materials than were medium mineralized waters.. With medium mineralized waters, the surface of the material was quickly carbonated, thus reducing potential exchanges with water.

The addition of CO_2 (aggressive CO_2) to migration test water made it more aggressive, but waters containing free aggressive CO_2 were unstable in contact with the atmosphere. The use of unstable water in the test protocol may result in greater scattering of test results if no precautions are taken to avoid escape of CO_2 during preparation.

The presence of silica in test water has a major effect on aluminium leaching, mainly for soft waters. During their commissioning and service, cement-based materials come into contact with natural waters, which, for most of them, contain dissolved silica.

REFERENCES AND BIBLIOGRAPHY

ANSI/NSF (1997), Standard 61 – 1997b, *Drinking Water System Components – Health Effects*, American National Standards Institute.

AWWA/DVWG-Technologiezentrum Wasser (1996), *Internal Corrosion of Water Distribution Systems*, second edition, AWWA Denver.

Bailey, R.J., Jolly P.K. and Lacey R.F. (1986), Domestic water use patterns, *WRC-report TR 225*.

BS 7766 (1994), *Specification for Assessment of the Potential for Metallic Materials to Affect Adversely the Quality of Water Intended for Human Consumption*, British Standards Institution, London.

Conroy, P.J. and Oliphant, R. (1991), Deterioration of water quality. The effects arising from the use of factory applied cement mortar linings, *WRC Report N DoE* 2723-SW.

DIN (1999), Standard 50931-1 *Corrosion of metals – Corrosion tests with drinking water, Part 1: Testing of change of the composition of drinking water*.

European Commission (2000). Co-normative research on test methods for materials in contact with drinking water, report EUR 19602 EN.

European Consortium (P. Buijs *et al*.) (1998), Developing a new protocol for the monitoring of lead in drinking water, European study.

Franqué, O, Meyer, E. and Sauter, W. (1995), Operation of a test rig to assess the suitability of alloys in different types of water. *Proceedings of International Corrosion Workshop and Seminar*, Internal corrosion in water distribution systems, Chalmers University of Technology, Göteborg.

Kuch, A. (1984), Untersuchungen zum Mechanismus der Aufeisenung in Trinkwasserverteilungssystemen. PhD dissertation, Universität Karlsruhe, Germany.

Kuch, A. and Wagner I. (1983), A mass transfer model to describe lead concentrations in drinking water, *Water Research* **17**, 1303–1307.

Kuch, A., Sontheimer, H. and Wagner, I. (1983), Die Messung der Aufeisenung im Trinkwasser – Ein neues Verfahren zur Beurteilung von Deckschichten in schwarzen Stahlrorhen, *Werkstoffe und Korrosion*, **34**, 107–111.

Meyer, E. (1980). Beeinträchtigung des Trinkwassergüte durch Anlagenteile der Hausinstallation-Bestimmung des Schwermetalleintrags in das Trinkwasser durch Korrosionsvorgänge in metallischen Rohren, *DVGW Schriftenreihe Wasser*, Nr. 23, 113–131.

Meyer, E. (1981), *Gesetzmäβigkeiten des Eintrages von Schwermetallen in Trinkwasser*. Schiftenreihe Verein Wa Bo Lu 52, 9–10, Gustav Fischer Verlag, Stuttgart.

Oliphant, R.J. (1992), Effectiveness of water treatments in preventing contamination from a leaded brass, *Foundation for Water Research Report FR0338*.

Sauter, W. (1995), *Bewertung des Betriebes einer Versuchsanlage zum Vergleich den Metallabgabe von Installationwerkstoffen. Abschlussarbeit im Weiterbildenden Studium Korrosionsschutztechnik*, Märkische Fachhochschule, Iserlohn.

Sauter, W., Meyer E. and Franqué, O. (1996), *Beurteilung von Armaturenwerkstoffen auf ihre Eignung im Trinkwasserbereich*, SHT 61, 10, S 97–100, 105.

Van den Hoven, Th. J.J, and van Eekeren M.W.M. (1988), *Optimal Composition on Drinking Water, Kiwa-report 100*, Nieuwegein.

Van den Hoven, Th. J.J, Baggelaar P.K. and Ekkers G.F. (1990), *Koperafgifte door drinkwaterleidingen, Kiwa-report 111*, Nieuwegein.

Wagner, I. (1992), Internal corrosion in domestic drinking water installations, *Journal Water SRT – Aqua* **41**, 219–223.

Werner, W. (1992), Untersuchungen zum Mechanismus der Flächenkorrosion in Trinkwasserleitungen aus Kupfer, PhD dissertation, Universität Karlsruhe, Germany.

Werner, W. *et al.* (1994), Untersuchungen zur Flächenkorrosion in Trinkwasserleitungen aus Kupfer, *Wasser, Abwasser* **135**, 92–103.

WHO (1998), *Guidelines for Drinking Water Quality*, Second edition, Volume 1, *Recommendations*, World Health Organization, Geneva.

Index

Note: Page numbers in **bold** refer to tables and those in *italics* refer to figures.

Analytical Methods for Drinking Water: Advances in Sampling and Analysis Edited by P. Quevauviller and K. C. Thompson © 2006 John Wiley & Sons, Ltd. ISBN: 0-470-09491-5

With thanks to Geraldine Begley for creation of this index.