

**ESTABLISHMENT OF A LABORATORY ACCREDITATION
SYSTEM WITHIN THE MINING INDUSTRY**

Presented in partial fulfilment of the requirement for the Degree of Master in
Science in Environmental Protection.

By

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DEDICATION

To Ger, Ruairi and Oisin, for all their support.

DECLARATION

This thesis has not been previously submitted to this or any other college and, with acknowledged exception, is entirely my own work.

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ABSTRACT

Both metals and minerals are of pivotal importance to modern lifestyles and this situation will continue for the foreseeable future. Despite this obvious need for metals, people have a fear of the polluting emissions caused by the mining industry. Legislation now exists which will help to generate trust among the public. But compliance with regulations is only as good and as credible as the accuracy and the quality of the analysis. Laboratory Accreditation is a formal recognition that a laboratory is competent to carry out specified tests. The National Accreditation Board is the competent authority in Ireland to carry out accreditation in accordance with European Standards. This study will identify the need for a laboratory accreditation system within the mining industry and propose a schedule for implementation of same.

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CHAPTER ONE

INTRODUCTION

1:0 INTRODUCTION:

In general, the mining industry has a poor public image. In Ireland, the industry has had a bad press and many aspects of mining have been subject to bitter attacks, (Finlay 1991). Mining in the past, through lack of regulation, lack of knowledge of environmental consequences, careless or ill-conceived practices, or simple greed, has polluted its immediate environment to some degree. There is also public perception of inevitable pollution, associated with mining, that generates a genuinely held fear of the unknown and consequently provokes objection, (Robinson 1994). However the risks from mining are quantifiable, manageable, and preventable. Modern mines deal with environmental matters as an integral part of their operations, by ensuring that environmental controls and remedies are in place, before, during and after mining activities. (Finlay 1991). Both metals and minerals are of pivotal importance to modern lifestyles and this situation will continue for the foreseeable future.

Since May 1995, emissions from all new mining and minerals developments come directly under the umbrella of the Environmental Protection Agency (E.P.A). The EPA was established in 1992 by the Irish government as an independent body dedicated to environmental protection. The evolution of the EPA has established a new era for the management and protection of the environment, and helps to generate a feeling of trust among the public.

The mining industry must be seen to operate within a trustworthy legislative framework which defines allowable limits for emissions, to ensure protection of people and the environment.

Having defined these limits, monitoring and compliance can be ensured by both regulatory and voluntary means.

All mines have laboratories for

- (a) process and quality control to ensure and maximise the economic success of the mining company,

- (b) self monitoring to ensure compliance with regulations regarding emissions to the atmosphere.
- (c) analysis of the effects of emissions on flora and fauna.

Laboratories must submit data to State and Municipal agencies to demonstrate compliance with relevant laws and regulations. These agencies require that this data is generated under adequate quality assurance programmes. Accreditation enables an organisation to put in place quality systems which can be operated efficiently.

Laboratory Accreditation can be defined as;

" verification by a competent, disinterested third party that a laboratory possess the capability to produce accurate test data, and that it can be relied upon in its day to day operations to maintain high standards of performance."

(Dux, 1990)

The words "competent", "accurate", "reliable", "high standards" are the key words in this definition. These words will be repeated over and over again throughout this report, because, without accurate results from a competent laboratory, any report will be meaningless.

The ever increasing need for metals and the ability of modern mining and processing methods to develop low grade ore bodies economically, has placed increased strain on the environment at a time when demands for high environmental standards are also increasing. The higher environmental profile attached to modern mining is linked not only to social acceptability, but also to legal requirements in many countries, (Johnson et al 1994). The mining industry has a high environmental compliance monitoring requirement with respect to emissions to air, water, soil and herbage. This gives rise to the need for accurate, reliable laboratory data.

Accreditation under an independent national scheme ensures quality and accuracy and hence credibility. The key elements of a laboratory accreditation system are demonstrated in the Flow diagram, Figure 1.1

Figure 1.1

1. Need for reliable data

implies

2. Rigorous quality assurance programme

achieved by

3. Accreditation

results in

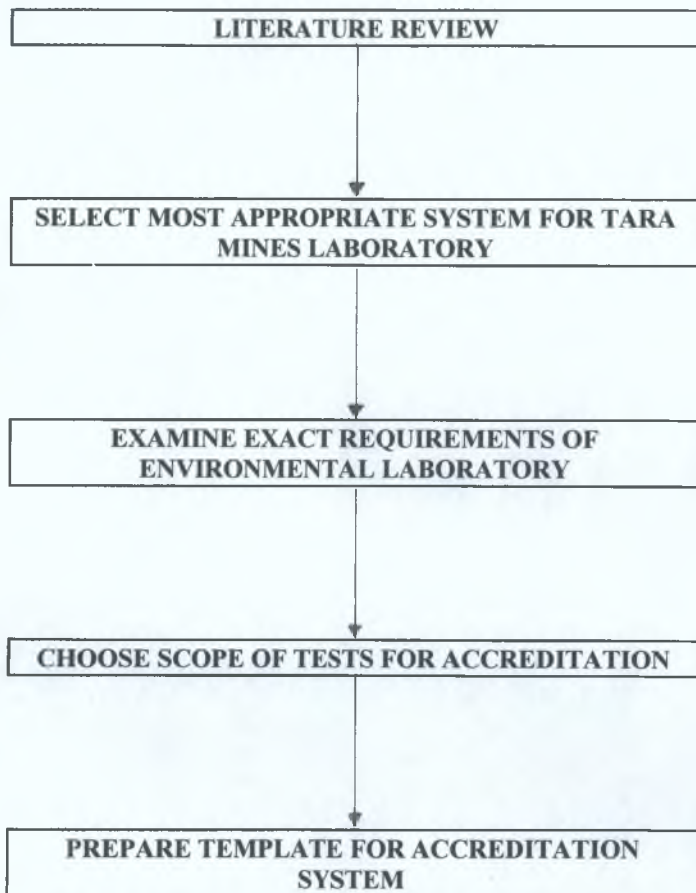
4. Credibility

1:1 Aims and Objectives:

The aim of this study is to demonstrate the need for a laboratory accreditation system within the mining industry and to identify systems of accreditation through a literature review.

The most suitable system for the Environmental laboratory at Tara Mines will then be selected and a basic plan and implementation schedule will be prepared. The aims and objectives are set out in Figure 1.2.

FIGURE 1.2 AIMS AND OBJECTIVES.



CHAPTER TWO

LITERATURE REVIEW

2:1 What is accreditation?

Cullen, (1992) states that Laboratory accreditation is a formal recognition that a laboratory is competent to carry out specified tests. According to Kibblewhite, (1993) accreditation may be the largest development project a laboratory will encounter in terms of complexity as well as cost. Accreditation, which is already in use throughout the European Union, is an indispensable guarantee of the competence of laboratories and certification bodies. (Anon, NAB literature 1995)

2:2 Reasons for accreditation

Kibblewhite, (1993) lists some of the reasons for a laboratory applying for accreditation as being;

- Accreditation is an entry requirement for the environmental testing market.
- Accreditation provides a template for more effective control over operations and their quality.
- Accreditation is something of a prize- a tangible organisational goal.
- Accreditation is an acceptable alternative to dual monitoring.

Dempsey, (1993) states that

"the reliability and usefulness of any test report depends critically on the competence of the laboratory carrying out the tests. Consequently, many countries operate national accreditation schemes for testing laboratories, to assure the users of test reports and certificates of the quality of the service provided".

More and more it is being found that to satisfy clients needs, managers must establish a rigorous quality assurance programme as defined by an outside organisation (Dux, 1990).

Dallas, (1991) maintains that accreditation status for company laboratories would be an acceptable alternative to dual monitoring (i.e. monitoring by both the regulatory body and the operator.) There are also a number of legal or regulatory bodies who are

presently highlighting the need for accreditation, for example the Environmental Protection Agency Act 1992, section 66 deals with the Establishment of an Accreditation Scheme.

(1) (a) The agency may, for the purposes of assessing analytical performance and ensuring the validity and comparability of environmental data, establish, or arrange for the establishment of, an analytical quality control programme involving its own laboratories, laboratories provided and operated by local authorities, and such other laboratories as it deems appropriate from which data are submitted to the Agency in connection with the performance of any of its functions.

(b) The Agency may require any such laboratory to furnish it with such data as it may request for the purposes of any such programme.

(c) Without any prejudice to the generality of paragraph (a), the Agency may establish different analytical control programmes for different laboratories or for different tests.

(d) The Agency may require any laboratory which supplies environmental data to the agency or in connection with any function under this Act to be accredited in accordance with Irish Standard I.S/En 45001: 1989- GENERAL CRITERIA FOR THE OPERATION OF TESTING LABORATORIES- or equivalent and with such other or further standards as may be set, from time to time, by the National Standards Authority of Ireland or equivalent standards.

This legislation, therefore, requires that laboratories who submit data to the Environmental Protection Agency, must ensure that the data has been generated under strict quality controls. This can be achieved when a system of accreditation is established.

The European Commission document "A global approach to Certification and Testing" (1989), contains the recommendation that " in order to generate confidence and mutual trust as between national authorities, member states should be required when implementing community legislation to notify only those laboratories and bodies which can demonstrate conformity to the EN 45000 series " (Dempsey, 1993).

It is not surprising therefore to find that the Environmental Protection Agency Act (1992), section 66(2) has made provision to require laboratories supplying environmental data to be accredited to EN 45001.

A number of environmental management systems recognise the need for accreditation also. The Environmental Impact Statement (Anon.1992 Galmoy) prepared for the Galmoy mine project recognises the rapidly developing area of environmental protection with the development of a comprehensive management system. In Chapter 2.11 it states;

"In establishing this E.M.S, the company's objective is to prepare for accreditation to a national or international standard when such a standard is in place".

A system of accreditation would also satisfy the requirements of BS 7750 (1992). In the introduction to BS 7750 it states;

" Organisations of all kinds are increasingly concerned to achieve and demonstrate sound environmental performance. They do so in the context of increasingly stringent legislation, the development of economic and other measures to foster environmental protection, and a general growth of concern about environmental matters. This British Standard specifies the elements of an environmental management system, intended to apply to all types and sizes of organization. A system of this kind enables an organisation to establish procedures to set an environmental policy and objectives, achieve compliance with them, and demonstrate such compliance to others. The standard is also intended to support certification schemes".

The Standard, EN 45001 (1989), was drawn up with the objective of promoting confidence in those laboratories which conform to it. The criteria set out in this standard are those to which laboratories should conform and which should be used by

accreditation bodies in its assessment of laboratories. This European Standard specifies general criteria for the technical competence of testing laboratories.

In the Irish standard, I.S 310 (1994) on Environmental Management Systems (EMS), it is established that achieving and demonstrating sound environmental performance is accomplished by operating a model system which can be subject to assessment. Of the eight elements of an EMS, one is the "voluntary implementation supported by certification to a recognised standard".

NAMAS, The National Measurement Accreditation Service was formed in 1985 in the U.K. NAMAS accredited laboratories meet the requirements of EN 45001 and ISO Guide 25.

2:3 The National Accreditation Board

In 1985, at a request from government, a National Accreditation Scheme was started in Ireland. The Irish Laboratory Accreditation Board (ILAB), as it was then known, was an autonomous unit of the National Standards Authority of Ireland (N.S.A.I). Accreditation by ILAB means that a laboratory has been thoroughly assessed by a team of specialists and has been recognised by an independent national body as competent. ILAB is supervised by an independent body of experts in laboratory testing drawn from a wide range of different technical fields.

In 1994, ILAB became the competent body for accreditation of certification bodies and so became ICLAB, The Irish Certification and Laboratory Accreditation Board. ICLAB underwent a further name change in January 1995 when the board became independent of the N.S.A.I and is now known as The National Accreditation Board. (Anon. 1995 NAB)

2:3.1 Functions of The National Accreditation Board

- It is the Irish national body for the accreditation of laboratories and certification bodies. These accreditations are carried out in accordance with the harmonised European Standards of the EN 4500 series.
- It has statutory responsibilities for the enforcement of *Good Laboratory Practice* under *S.I no.4 of 1991*. (European Communities (good laboratory practice) regulations, 1991)
- Most recently it has been designated as the competent Body (registration body) under the EU *Eco-Management and Audit Scheme Regulations (EMAS)*. (EC Eco-Management and Audit Scheme. EMAS. Council Regulation (EEC) No. 1836/93 of June 1993).
- It is also responsible for the accreditation of Environmental Verifiers under the EMAS scheme.
(Anon.1995 NAB)

The criteria of the National Accreditation Board are in accordance with the recommendations of the International Organisation for Standardisation (ISO) Guide 25 and are consistent with the EN 45001 European Standard developed for the accreditation of laboratories by the European Commission.

2:3.2 Aims of the National Accreditation Board;

The main aims of the Board are;

1. To provide a national unified laboratory accreditation service.
2. To improve the quality and standard of testing and calibration in Ireland.
3. To eliminate multiple assessments - particularly when goods cross national frontiers.
4. To negotiate memoranda of understanding with the national accreditation schemes of other countries.
5. To provide publicity for accredited laboratories through publication of a directory of such laboratories.

(Dempsey, 1993)

The National Accreditation Board Scheme is an important instrument of government policy for the improvement of the quality image of Irish products abroad and particularly within the European Community. In 1993, the Board was accepted into full membership of the multilateral mutual recognition agreements of the Western European Laboratory Accreditation Co-Operation (WELAC) and the Western European Calibration Co-Operation (WECC).

2:4 The requirement for Accreditation in the mining industry:

Finlay, (1991) gives an overview of the mining industry and says that, in general, the mining industry has a poor image. The terminology used is harsh and cold; pitting, stripping, blasting, waste piles, tailings and disposal are not words that convey any sense of concern or gentleness. In Ireland, the industry has had a bad press and many aspects of mining have been subject to bitter attacks. He goes on to say that the risks of harm from mining are quantifiable, manageable, and preventable. Modern mines deal with environmental matters as an integral part of their operations, by ensuring that environmental controls and remedies are in place, before, during and after mining activities confirming the acceptance of responsibility by the mining industry to people and the environment.

Johnson et al, (1995) comment on the progressive worldwide increase in metalliferous mining in recent years, underpinned by social, economic, and technological demand. The ever increasing need for metals and the ability of modern mining and processing methods to develop low grade ore bodies economically, has placed increased strain on the environment at a time when the demands for high environmental standards are also increasing. Since mining is, by its very nature, a destructive industry, attention has become focused on ways in which the environmental impact may be reduced or rendered temporary in nature. The higher environmental profile attached to modern mining is linked not only to social acceptability, but also to legal requirements in many countries.

Barbour (1995) talks about the products of the extractive industry. Both metals and minerals are of pivotal importance to modern lifestyles. This situation will continue for the foreseeable future in spite of the inroads made into some non-ferrous applications by plastics, ceramics and composites. Metals occur naturally in a wide range of stable concentrations in the ground, but unlike organic chemicals and plastics, metals generally cannot be degraded chemically or bacteriologically into

simpler constituents, such as carbon dioxide and water, which are relatively neutral environmentally.

Despite the obvious need for metals, people have a fear of mining, or rather a fear of the polluting emissions to land, air and water, caused by the mining process. This fear is understandable, and is easily exploited. To overcome these fears, the mining industry must be seen to operate within a trustworthy legislative framework which defines allowable limits for emissions to ensure protection of people and the environment. Having defined these limits, monitoring and compliance can be ensured by both regulatory and voluntary means. The key issue is one of Trust.

2:5 Environmental and legislative issues:

Since May 16th, 1995, emissions from all new mining and minerals developments come directly under the umbrella of the Environmental Protection Agency (E.P.A), in particular with regard to the provision of Integrated Pollution Control Licensing. (Anon, EPA 1994). The EPA was established in 1992 by the Irish government. It is an independent body dedicated to environmental protection. With the establishment of the EPA, a new era has commenced for the management and protection of Ireland's environment. Section 66 of the Environmental Protection Agency Act, 1992 dealing with the establishment of an accreditation scheme has already been mentioned in Chapter 2:1. Compliance with regulations is only as good and as credible, both to the EPA and to the public at large, as the accuracy and quality of the analysis. Accreditation under a scheme such as that set up by the National Accreditation Board, ensures quality and accuracy and hence credibility.

2.6 Mining laboratory services:

Planning conditions attached to any mining project will require a high compliance monitoring regime with respect to water, air, herbage and soil. Therefore, accurate, reliable data must be obtained. Within any manufacturing industry, the data being produced by the laboratory is essential for the smooth running of the operation. The laboratory is the cornerstone of any quality control programme and so the data generated must stand up to scrutiny. Some of the services provided by a mining laboratory include;

- Routine analysis of water prior to discharge to ensure compliance with discharge limits.
- Analysis of dust emissions from stack dryers.
- Analysis of ambient dust filters.
- Analysis of herbage and soil for metals uptake.

- Analysis of blood Lead levels in the workforce.
- Research into mine tailings rehabilitation. This includes analysis of small animals to monitor heavy metals uptake for food chain analysis, also analysis of herbage to select the most suitable strain to ensure the long term stability of the tailings surface.

This is all high cost analysis giving results which may be questioned if the laboratory is not accredited. This in turn may lead to high cost verification analysis.

CHAPTER THREE

SETTING UP AN ACCREDITATION SYSTEM

3:0 Setting up an accreditation system:

Setting up an accreditation system within a laboratory should follow a defined route over a scheduled timeframe. The most important key areas to consider are;

1. General organisation and staff
2. Quality system
3. Testing and measuring equipment
4. Calibration
5. Test methods and procedures
6. Environment
7. Handling of items to be tested
8. Records
9. Test reports
10. Complaints

This is based on the General Criteria of Competence for testing laboratories. (ILAB P1 1986). Each of these topics will be examined separately in the following chapter.

3:1 General organisation and staff:

All staff shall be technically competent for the functions they undertake. Information on the relevant qualifications, training, and experience of staff shall be maintained by the laboratory.

The details of the organisational and staffing arrangements, and the extent to which they are formalised will depend on the size of the laboratory and its range of activities. For certain activities, there may be nationally or internationally recognised minimum qualifications or training requirements. In some cases, lack of qualifications or formal training may be adequately offset by appropriate experience or supervision. In the case where a laboratory forms part of a larger company, it should be ensured that the laboratory is free from organisational pressures that may influence the outcome of tests. It is essential that the laboratory is organised in such a way that all employees are aware of the extent and limitations of their area of responsibility. The testing laboratory shall have a Technical Manager who has overall responsibility for the technical operations of the laboratory. A person or persons having responsibility for quality assurance within the laboratory shall be designated by the laboratory management and have direct access to the top management. (ILAB P1 and P3 1986).

3:1.1 Quality Assurance

Good Laboratory Practice or " Quality Assurance" is the essential organisational infrastructure that underlies all reliable analytical measurements. It is concerned with achieving appropriate levels in matters such as;

- Staff training and Management
- Adequacy of the laboratory environment
- Safety, storage, integrity and identity of samples
- Record keeping
- Maintenance and calibration of instruments
- Use of properly documented methods

In recent years, these practices have been codified and formally recognised as essential. However, it should be noted that the prevalence of these favourable conditions by no means ensures the attainment of appropriate data quality.

(Analyst, 1995)

The establishment and maintenance of a good quality assurance programme requires the allocation of human and financial resources.

3:1.2 Commitment of staff to the programme

With regard to human resources, in order that laboratory personnel will be committed to the programme, it is important to;

1. Communicate management's commitment to the programme.
2. Be sure the Quality Assurance officer has a position of high visibility within the organisation, and communicate the fact that he/she has management's backing and authority.
3. Educate employees regarding the objective of the programme and prepare a written description of the programme, so that there is little doubt regarding the content of the programme.
4. Most important is to involve all employees in the definition and establishment of the programme. Request their suggestions and comments on all proposed procedures. The goal should be to arrive at consensus on the procedures to be followed to achieve the required results.

In practice, the employment of well educated, well trained and motivated staff is the key to the successful implementation and maintenance of any accreditation scheme. (Dux, 1990)

3:2 Quality System:

The word "quality" is one of those words that may have many different meanings, depending on the context. One definition of the quality of an analytical result that is relatively unambiguous, scientifically correct and easy to understand is;

"The quality of a result is equivalent to its accuracy, that is, the degree to which a result approaches the "true value" of the thing being measured or determined."
(Dux, 1990)

Unfortunately the " true value " of the analyte is seldom known. However, by analogy with results obtained on materials of known composition, we can at least estimate the accuracy of a result on an unknown.

A Quality System consists of documented laboratory activities aimed at producing accurate work and a high quality work product. Any laboratory must operate an internal quality system appropriate to the type, range and volume of work performed. This Quality System will be formalised in a **Quality Manual** which is available for use by the laboratory staff.

3:2.1 Quality Manual

The Quality Manual shall define in detail;

- The scope of operation of the laboratory (i.e. the range of tests being performed)
- The organisation of the laboratory
- Terms of reference of senior technical personnel
- Approved signatories
- Inter-relationship of management, technical operations, support services and quality control

- The laboratory's quality policy statement
- General quality assurance procedures
- Reference to quality assurance procedures specific for each test, as appropriate
- Reference to proficiency testing, use of reference materials
- Satisfactory arrangements for feedback and corrective action whenever testing discrepancies are detected
- Procedures for dealing with complaints

(ILAB P1, 1986)

The Quality Manual will set out all the arrangements necessary to ensure the quality of the services provided by the laboratory. The quality manual should be a key to the totality of the activities for which the laboratory is accredited or seeking accreditation.

3:3 Testing and Measuring Equipment:

Developing technology has led to sophisticated new tests dependent on integrated instrumentation, and the performance of these tests can be influenced by drifts in instrumentation performance. The laboratory therefore, shall hold or have access to all equipment required for the correct performance of the tests and measurements for which it is accredited.

3:3.1 Equipment information

All equipment shall be;

- Uniquely identifiable- for example, serial number or equipment number.
- Operated by staff that are authorised to do so and have up to date instructions available on the use of such equipment.
- Properly maintained to ensure adequate protection from deterioration.

- Withdrawn from service if suspect results are given, or shown by calibration to be defective. Equipment must then be clearly labelled "Out of service" and must not be re-introduced until satisfactorily repaired or shown by calibration to be within specifications.
- Shall have maintenance records including;
 - name of item of equipment
 - manufacturers name and type identification
 - serial number or unique identification number
 - date received
 - date in service
 - current location
 - details of maintenance carried out
 - history of any damage, defects

For measuring equipment also include

- date of last calibration
- maximum permitted time between calibrations
- calibration reports

(ILAB P1, 1986)

3:4 Calibration and Quality Control:

In order to ensure the continued accuracy of an instrument it must undergo an accuracy check and if necessary, adjustment at regular intervals. In other words, it must be Calibrated regularly. Calibration, is the set of operations which establish, under specified conditions, the relationship between the values indicated by a measuring instrument and the corresponding known values of the quantity measured.

3:4.1 Reasons for Calibration

In the context of ensuring confidence in measurements, the main reasons for calibration are;

1. To prove that the instrument is working.
2. To verify that the instruments performance specifications have been met over the period since it was last checked.
3. To optimise, realign, adjust or create an error chart for the instrument so that it can be used, and assumed to meet its specification over the coming period, before it is checked again. (Anon.Forbairt 1994)

Calibration is not a bureaucratic exercise. Its prominent appearance in published standards for quality management systems (e.g. ISO 9000 series), where the emphasis is placed necessarily on the external manifestations such as record keeping and labelling, may sometimes give this impression. While an effective calibration programme is necessary to control the instrumentation, the basic purpose of calibration is to give confidence in measuring results. Instruments need to be calibrated whether or not a formal quality management system is in operation. Calibration of a measuring instrument will ensure that it agrees with the reference standard against which it was calibrated. In turn, the reference standard must be verified by calibration against a standard of yet higher accuracy. This process is extended so that all measurements can ultimately be traced back to a common agreed standard.

3:4.2 Traceability

Traceability is the term used whereby the property of a measurement can be traced back via an unbroken chain of calibrations, to an agreed national or international standard. Traceability is essential to ensure compatibility of measurement results. Traceability implies not just the use of authenticated standards but the use of approved procedures at each stage of the calibration chain. The overall programme of calibration of equipment shall be designed and operated so as to ensure that wherever applicable, measurements made in the testing laboratory are traceable to national and

international standards of measurement where available. Where traceability to national or international standards of measurement is not applicable, the testing laboratory shall provide satisfactory evidence of correlation or accuracy of test results (e.g. by participation in a suitable programme of interlaboratory comparisons.) Measuring and testing equipment used in the laboratory shall be calibrated where appropriate, before being put into service and thereafter in accordance with a documented programme. Reference standards shall be calibrated by a competent body to provide traceability to international measurement standards. The existence and effective operation of an overall programme for controlled calibration of instruments is vital to all laboratories engaged in testing.
(EN 45001, 1989)

3:4.3 Frequency of calibration

The frequency of calibration depends on;-

- The nature of the instrument and its ruggedness.
- The frequency of use of the instrument.
- The testing environment (i.e. dust, vibration.)
- The demands of the analytical methodology. (Dux, 1990)

The procedures for calibrating all instruments should be recorded and stored in a Calibration Methods Notebook. The traceability of all measurements is based on;

1. The Internal Calibration System and
2. The External Calibration System.

3:4.4 The Internal Calibration System

The internal calibration system is concerned with the relationship between the laboratories reference standards and its working instruments.

3:4.5 The External Calibration System

The external calibration system concerns the traceability between the laboratories reference standards and international measurement standards.

3:4.6 Quality Control System

The laboratories Quality Control System is examined under the heading of Calibration. Quality Control is the term used to describe the practical steps undertaken to ensure that analytical data are adequately free from error. Inter-laboratory calibration is an essential component of a laboratories quality control programme. It supplements the laboratories own intra-laboratory quality control system as a means of detecting and guarding against errors which would otherwise lie undiscovered.

3:4.6.1 Proficiency Tests

Proficiency tests play a key role in demonstrating the need for remedial action in laboratories with long term problems in achieving data of appropriate quality. Successful schemes demonstrate, that participants have the ability to produce data of a given quality on the occasions of the tests and hence have the potential to do so on other occasions. The ISO has recently published a draft protocol on harmonised Proficiency Testing which sets out minimum procedures for organisations running Proficiency Testing schemes.

Proficiency Testing is defined by the ISO draft protocol as

"the system for objectively checking laboratory results by an external agency. It includes comparison of a laboratories results at intervals with those of other laboratories, with the main objective being the establishment of trueness."

Proficiency testing provides an independent and objective means of assessing and confirming the continuing reliability of laboratory data. (Concannon, 1993)

3:4.6.2 Benefits of Proficiency Testing

- provides an objective and independent assessment of quality
- compares performance with peer laboratories
- provides technical advice
- provides information on methods
- improves accuracy
- supports accreditation
- assists marketing. (Bathie, 1993)

3:4.6.3 Limitations of Proficiency Testing

- necessarily restricted in the scope of materials and determinands that can be prepared and circulated for testing. The performance of a laboratory in a given test often has to be taken as an indication of its capabilities for a wide range of related analyses.
- samples analysed are usually identifiable as check samples and may be analysed with more care than usual-hence the standard of accuracy achieved is not necessarily typical of the laboratory's routine operation.
- They are repeated over a long time scale and therefore cannot indicate the short term variations in quality that can occur within laboratories.
- They function as good indicators of overall data quality, but they do not identify clearly the sources of errors and thereby point to effective remedies. (Analyst, 1995)

3:4.6.4 Quality control procedures

In the analytical laboratory some typical quality control procedures which are used include;

- Blanks
- Standards
- Spiking
- Quality control check samples
- Control charts
- Replicate analysis
- Blind samples

Preventative Quality Control procedures minimise the risk of errors occurring. They include;

1. The use of a good documentation system.
2. Regular maintenance and calibration checks on equipment.
3. System of validation.
4. Good laboratory design.

3:4.6.5 Documentation

Documentation is essential for the standardization of methodology, reproducibility of methods, effective analysis and traceability of results. It is imperative that all documentation be accurate, complete, accessible and available to all users.

Documentation requirements include;

- Standard Operating Procedures
- Equipment operating procedures
- Reagent records
- Test records
- Quality control records and analyses

- Equipment maintenance records.

(Malic, 1993)

3:5 Test Methods and Procedures:

In the analytical laboratory, the analytical method or test method is the medium by which management informs the workers of the procedures to be used in performing the work. In many laboratories, the methods used are not documented, or if they are, they may be in a very sketchy form. New workers are simply trained in the methods used by experienced workers with little reference to a written copy of the method.

The hazards of this type of operation are obvious. If methods are not documented and available to the analyst, the possibility of intentional or unintentional variations in the method is always present. Since management is ultimately responsible for the quality of analytical results it is essential that workers understand the importance of the written method.

3:5.1 Use of methods;

There are three general principles involved;

1. All methods used in the laboratory should be in written form. The methods should be collected in a "Methods Manual" and be available to workers at all times.
2. All methods used in the laboratory should be authorised for such use by management, and files kept of documents indicating that each method has been so authorised.
3. All employees should be informed that unauthorized methods may not be used in the laboratory. (Dux, 1990)

3:5.2 Sources of analytical methods

In general, the four sources of analytical methods are:

(1) Standard Methods

Standard methods are by far the best methods to use. These methods are set by standard setting organisations such as " The American Society for Testing and Materials " (ASTM) or "The Association of Official Analytical Chemists " (AOAC) or "The British Standards Institute " (BSI). These methods are subjected to intensive investigation by many individuals and laboratories before being awarded the status of "Standard" and therefore are usually the best that can be had. Wherever possible Standard Methods should be used in the laboratory because they have been thoroughly tested and are widely accepted.

(2) Official Methods

These methods apply to methods mandated to be used by government organisations in cases of analysis for compliance with government regulations. Laboratories involved in this kind of work usually have no choice but to use these methods.

(3) Literature Methods

These methods come from general purpose analytical journals, or specialised journals and from literature pertaining to certain instruments. Caution should be exercised when using literature methods and a thorough validation study should be made of any such method.

(4) In-house developed methods

Caution should be exercised with in-house methods also. A thorough validation study should be carried out and the method authorized by management before being introduced.

(Dux, 1990)

In general, methods which are accepted and taken as standard or national methods will be used. Where In-House methods are used, or non-standard methods, the documentation will include the following information; (ILAB P3, 1986)

- (a) identification of the test item concerned
- (b) identification of any specification against which the item is to be tested
- (c) characteristics and design criteria to be inspected or tested, including any tolerance limits prescribed
- (d) layout and interconnection of test equipment and test items
- (e) sequence of operations and verifications
- (f) environmental and other conditions maintained, including tolerances
- (g) any special instructions for handling, preparation, inspection or testing (e.g. special handling of fragile test items)
- (h) any special precautions which must be taken to ensure safety of personnel, or to prevent damage to test items and measuring equipment.

This information is normally needed in advance, by any laboratory, in order to undertake a given test properly, whether the methods or procedures are standard or non-standard.

All instructions, specifications, manuals and reference data relevant to the work of the laboratory shall be maintained up to date and be readily available to staff.

Documented instructions shall be available ;

- for the operation of all relevant equipment

- for handling and preparation of test items
- and on standard testing methods

where the absence of such instructions may adversely affect the testing process. An appropriate checking technique, aimed at minimising the possibility of calculation or transcription errors shall be established. This will enable any such error to be detected and rectified prior to the issue of a final report.

3:6. Environment:

One of the most important factors in the analytical system impacting on the quality of analytical results is the physical facilities available in the laboratory. Controlled temperature, good lighting, adequate electrical supply and a pleasant working environment are necessary in today's laboratory. There are two general principles to be considered in relation to the environment ;

1. The need for a proper environment for optimum operation of equipment and instruments.
2. The need for a proper environment for optimum performance of the employees.

The environment in which tests are undertaken shall not invalidate the test results or adversely affect the required accuracy of measurement. Access to and use of all test areas shall be controlled as appropriate to their designated purpose. Adequate measures shall be taken to ensure good housekeeping in the laboratory, and shall include a programme of regular cleaning. Where non laboratory personnel are used for cleaning purposes, the arrangements should ensure that

- test items cannot be lost or damaged
- equipment is reasonably protected from accidental damage which might affect its performance,
- client confidentiality is not prejudiced

Protective clothing for staff and visitors should be provided where necessary.

With regard to the environment the following features should be considered;
(ILAB P3, 1986)

- Space, lighting and heating, adequately and solidly constructed benches, freedom from dust, fumes, noise and vibration, and electro-magnetic radiation.
- Sufficient space to provide for convenient and accurate operation.
- Control of temperature and humidity.
- controlled electrical service to protect from power surges and fluctuations.

3:7 Handling of items to be tested

Sample handling can be a rather technical job with its own needs for equipment and techniques. It is therefore recommended that sample receipt, log in and storage be carried out by trained personnel. The accountability objective of quality assurance requires that samples are handled in such a way as to avoid mix-up and to ensure that the sample when analyzed has undergone minimum chemical and physical change while in the laboratory. This may require that the sample be refrigerated or stored in special containers.

The testing laboratory shall operate a system for handling, storage and testing of items and samples which ensures that confusion cannot arise regarding the identity of any item or sample to which any measurement or record refers. The system shall include a procedure for recording the

- identity
- status
- and condition

of every sample at the time of its receipt. The laboratory shall provide adequate storage facilities to segregate items before and after testing. Clear rules shall be in place for the safe disposal of all test items. At all stages of storing, handling, and preparation for test work, precautions shall be taken to prevent any damage or deterioration of items which could affect the results. Any relevant instructions provided with the test sample shall be observed.

3:8 Records:

The quality assurance objective of *traceability*, that is, the ability to establish the actual data taken and the condition of the analytical system at the date an analysis was run, requires that this data be easily obtained. The records retained by the laboratory should contain enough information to allow the subsequent identification of possible sources of error and permit, where necessary, the repetition of tests under the original conditions. The retained records may be held in conventional (paper) or other form (computer system). All records, relating to staff, equipment and procedures shall be protected from loss, damage or misuse and be retained for an appropriate time. It is not necessary for all records to be retained in one central location. The Quality Manual should define how and where all records are stored.

3:8.1 Records system:

A recording system, to suit the particular laboratory shall be established. The following principles shall apply; (ILAB P1 and P3)

- A co-ordinated system shall be used throughout all the separate parts of the testing laboratory.
- All calculations and observations shall be recorded at the time when they are made.

- The records for each test shall contain sufficient information to permit, where necessary, satisfactory repetition of the test under the original conditions.
- Any significant departures from test specifications, work instructions or other technical procedures originally specified shall be recorded and justified together with authorisation where appropriate.
- Consideration should be given to the use of specially designed, pre-printed record sheets or log books wherever possible.
- All information should be adequately cross referenced to avoid the mislaying of important test data.
- Care should be taken to ensure that client confidentiality is not prejudiced by, for example, visitors to the laboratory or by non laboratory personnel involved in the repair, maintenance, or cleaning of the laboratory or its equipment.

3:9 Test reports:

The analytical report is the final product of the laboratory and is often the only contact the laboratory has with its clients. It is important that the report be complete, accurate and easily understood. (Dux, 1990)

1. The introduction to the report should include;
 - name, address, and phone number of the laboratory that performed the analysis.
 - name and organisation of the client. Reports go to individuals, not to organisations so it is important to have a contact persons name.
 - date and time the sample was received and the date report was issued.
 - name of the person who took the sample.
2. Include in the main body of the report;

- the results of the analyses that were performed.
 - the laboratory assigned unique sample number.
 - the clients sample number or other code.
 - avoid abbreviations. The analyst may know what they stand for, but assume that the client does not.
 - actual numerical result of the analysis.
 - units of concentration.
 - assign a code number to each result which designates the analytical method used and the analyst who ran the analysis. This can be useful for tracing questioned data.
3. Show the name, title, and signature of the laboratory supervisor on the bottom of the report. This is a vital part of the report as it shows that the signatory has reviewed the results, approves them and accepts responsibility for their quality.
 4. Where a report consists of more than one page, number each page using a format such as " page x of y ". This enables a client to tell immediately if a page is missing or not.

The work carried out by the testing laboratory shall be covered by a test report which accurately, clearly, unambiguously and objectively presents the test results and all relevant information. In the event of circumstances coming to light which cast doubt on the validity of results given in a test report, the testing laboratory shall notify the client promptly in writing. (ILAB P1 and P3, 1986)

3:10 Complaints:

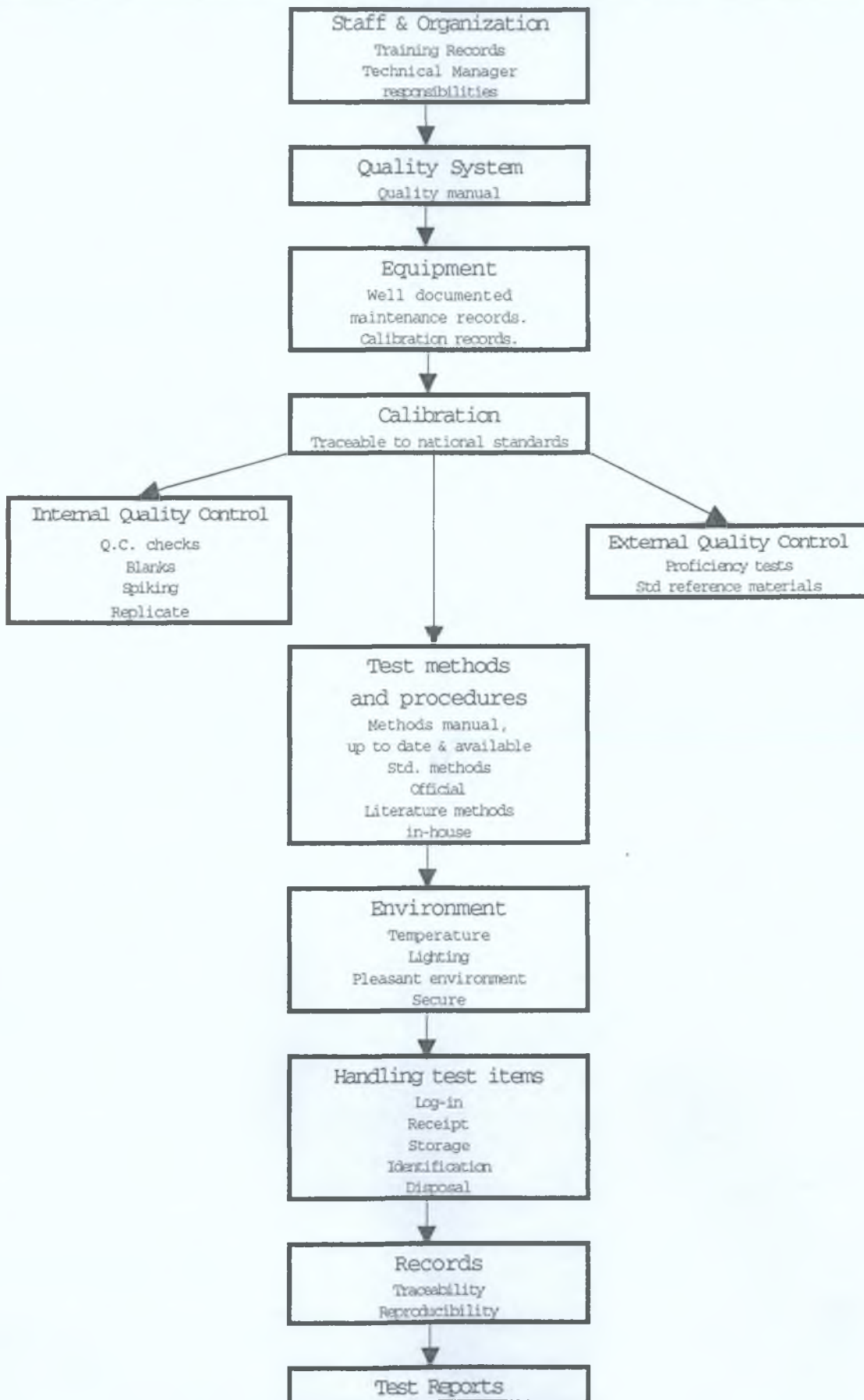
The laboratory shall have documented policy and procedures for the resolution of complaints received from clients. A record shall be maintained of all complaints and of the actions taken by the laboratory. Where a complaint raises doubt concerning the laboratory's compliance with laboratory policy or procedure, or otherwise, the laboratory shall ensure that those areas of activity and responsibility involved are promptly audited. (ILAB, P1)

Where the audit findings cast doubt on the correctness or validity of the laboratory's calibration or test results, the laboratory shall immediately notify, in writing, any client whose work may have been affected.

A Flow Diagram outlining the major aspects involved in setting up an accreditation system is given in Figure 3.1.

SETTING UP AN ACCREDITATION SYSTEM

Fig. 3.1



CHAPTER FOUR

PROPOSAL FOR SETTING UP AN

ACCREDITATION SYSTEM AT

TARA MINES ENVIRONMENTAL LABORATORY

4:0 Proposal for setting up an accreditation system at the Tara Mines Environmental laboratory.

Having demonstrated the need for an accreditation system and decided that the approach taken by the National Accreditation Board was the most suitable, the following chapter will endeavour to address specifically the situation at the Tara Mines laboratory.

The Tara Mines laboratory is situated on site at Navan, Co. Meath. The laboratory has eleven employees under the supervision of a Chief Chemist.

The laboratory is divided into four sections;

- (1) X-Ray section
- (2) Wet Chemical section
- (3) Sample Preparation section
- (4) Environmental section.

There exists a natural division between the first three sections and the Environmental section. The X-Ray, Wet Chemical and Sample preparation sections are involved with the internal efficiency of the mining operation. These sections deal with various types of ore samples. For example;

- (a) Geology samples- analysed as part of the on going exploration process.
- (b) Process control samples- analysed on a daily basis as back up to an on-stream analyser, involved in the ore processing.
- (c) Shipment samples- Zinc and Lead concentrate samples which are shipped to smelters worldwide.
- (d) Oil samples- taken from various machines to be analysed for wear metals, flashpoint, dispersancy.

The Environmental laboratory, on the other hand is concerned with Environmental monitoring of water, air, soil, and herbage to demonstrate compliance to Local Authority regulations. It has a duty to the community and to the workers to ensure that all the regulations set down by the Local Authority are met. The Environmental Laboratory is responsible for analysing blood samples, taken at least annually from employees, for Lead analysis.

The mining industry must be seen to operate within a trustworthy legislative framework which defines allowable limits for emissions to ensure protection of people and the environment. These limits are well defined in the case of Tara Mines and must be monitored according to the regulations. Because the reliability and usefulness of any test report depends critically on the competence of the laboratory carrying out the tests (Dempsey ,1993), an accredited laboratory can demonstrate this competence.

This project, therefore will concern itself with setting up a system of accreditation at the Environmental Laboratory only.

Using the criteria set out in the ILAB publication P1, and already discussed in detail in Chapter 3, an effective system can be established when the following template is followed.

4:1 General organisation and staff:

The National Accreditation Board have made recommendations regarding general organisation and staff requirements.

- (1) The laboratory shall have a Technical Manager who has overall responsibility for the technical operations of the laboratory.
- (2) The laboratory shall also include a Quality Manager who has responsibility for the laboratory's quality system.

- (3) The laboratory shall have a supervisor responsible for the day-to-day running of the laboratory.
- (4) The laboratory shall have an adequate number of skilled staff trained in the principles and practice of measurement for the range of testing involved. The range of work performed in the Environmental laboratory includes;
 - (a) routine monitoring of discharge water, river water, potable water.
 - (b) air monitoring
 - (c) soil and herbage analysis
 - (d) blood Lead analysis.

The objective of the laboratory is to provide a quality and flexible service in its specialised skills of laboratory analysis of environmental samples. The laboratory's clients include the Environmental and Metallurgical departments and the Medical centre.

4:1.1 Chief Chemist

The Chief Chemist has overall responsibility for maintaining a high standard of quality in the everyday operations of the laboratory. The Chief Chemist is the "Technical Manager" of the laboratory and is responsible for providing the resources necessary for to meet the quality objectives. The Chief Chemist is one of the signatories who approves Sample Reports.

4:1.2 Quality Manager

The laboratory will appoint a Quality Manager who has overall responsibility for control of quality within the laboratory. Duties of the quality manager will include;

- ensuring that the requirements of the National Accreditation Board are met.
- quality assurance of work carried out within the laboratory.

- planning quality audits.
- evaluating their effectiveness.
- ensuring that the audit procedures are fully documented and that the results are formally recorded.
- ensuring that any corrective actions have been implemented in an effective and timely manner.
- ensuring that, when and if necessary, the audit procedures are amended/ withdrawn or newly issued.

4:1.3 Environmental Laboratory Supervisor

The Environmental laboratory Supervisor will be responsible for the day-to-day supervision of the laboratory. Duties will include;

- the organisation of work priorities and schedules.
- liaison with the Chief Chemist regarding modifications and improvements in procedures or methods of test.
- carrying out the tests to the established procedures.
- supervision of tests and personnel undertaking tests.
- liaison with the quality manager and such co-operation as required to ensure the policies and procedures outlined in the Quality Manual are met.

4:1.4 Laboratory Technicians

The technicians are responsible, under the direction of the Environmental Laboratory Supervisor, for;

- carrying out tests to established procedures.
- accuracy of results and calculations.
- completing of test worksheets and other laboratory records.
- input of results into the computerised information system.

4:2 Quality System.

Over the years, many methods and practices have been amended. Sometimes these amendments may not have been recorded in a formal way. It is essential that a quality system be established and formalised in a Quality Manual. The Quality Manual will define in detail all the arrangements necessary to ensure the quality of the services provided by the laboratory. The Quality Manual will be prepared in accordance with the requirements set out in the ILAB publication P1. (Refer also to Chapter 3:2 Quality System).

4:2.1 Scope of accreditation

Under the quality system, the laboratory must decide on the scope of tests for which to seek accreditation. The choice of tests included in the initial accreditation scope is crucial. As the analysis of river water samples constitutes the bulk of the work performed at the Tara Mines laboratory, it is suggested that initial accreditation will be sought for analysis of these samples only.

There are four categories of water which are tested on a daily basis in the Tara Mines laboratory.

- (1) Process or Reclaim water
- (2) Fresh water
- (3) Surface Drainage water
- (4) Potable water

- (1) Process water is continually recycled through the entire mine.
- (2) Fresh water is pumped from the river Boyne to the mine site. This water is used to supply the fire-fighting water system and may also be used as a source of potable water.

- (3) Drainage water is all the surface water from rainfall, natural springs and streams.
- (4) Potable water is supplied to the mine from Navan town mains water system and is used to service utilities and as drinking water.

Excess process water is either pumped out to a holding pond or discharged back into the river Boyne. At the river, the clear water flows into a 600mm manifold pipe which spans the full river width. There are spigots on the line which allow a uniform discharge and the recommended dilution of 100:1.

The volume of clear water discharged to the river Boyne is closely monitored and controlled. Meath Co. Council has imposed a low limit dilution ratio of 100:1 on the discharge. The average amount of water discharged to the river in a year is 6800 m³/hr and the maximum rate of discharge must not exceed 45m³/min.

The following emission limits apply to discharge water;

<u>Parameter;</u>	<u>Limit mg/l</u>
pH	between 6-9
Suspended solids	20
B.O.D	30
Zinc	2
Lead	0.5
Copper	0.5
Iron	1.0
Cadmium	0.2
Arsenic	0.5
Antimony	1.0
Cyanide	0.2
Chromium	1.0
Mercury	0.05

(Tara Mines water manual)

The discharge water is monitored daily for;

pH, suspended solids, Zinc, Lead,
Copper, Iron, Antimony and Cyanide

and values must not exceed the limits set out by the Local Authority. For this reason, selection of some of these parameters for inclusion in the initial scope of accreditation would be appropriate. Of the eight tests which are performed daily, it is recommended that half of these will be selected for initial accreditation.

The following four parameters are suggested;

- (1) Ph
- (2) Suspended Solids
- (3) Zinc
- (4) Lead.

4:2.2 Justification for the chosen scope;

(1) pH; Measurement of pH is one of the most important and frequently used tests in water chemistry. Practically every phase of water supply and wastewater treatment, is pH dependent. Because the abstracted water at Tara Mines is being discharged back into the river, it is important not to disturb the delicate balance of the water supply. Therefore pH measurement is necessary.

(2) Suspended Solids; Analyses of suspended solids are important in the control of biological and physical wastewater treatment processes and for assessing compliance with regulatory limitations. At Tara Mines, the solids content of the discharge water is strictly regulated. If the emission limit of 20 mg/l is exceeded, no water may be discharged until the solids content is lowered.

(3) Zinc and Lead: Tara Mines is a major Lead and Zinc mine. Inevitably there will be traces of these metals in the wastewater. The effects of metals in water can

range from beneficial through troublesome to toxic. The limits set for Lead and Zinc must be strictly adhered to, hence the need for daily monitoring of these metals.

4:3 Testing and measuring equipment:

Having decided on the scope of accreditation, the next area to look at will be the equipment to be used for analysis. The instrumentation in use at present in the environmental laboratory will be more than adequate for the chosen analysis.

An equipment file has been set up already and all relevant data pertaining to each piece of equipment is maintained in this file. All equipment is uniquely identified by a Tara Mines equipment number and labelled with this number. The type of equipment in use includes;

- (1) Varian Atomic Absorption Spectrometer AA300 with Atom Concentrator Tube and Background Correction facility. This will be used for Zinc and Lead analysis.
- (2) Orion model 520A pH meter with Automatic Temperature Compensator probe. This will be used for pH measurements.
- (3) Digitally controlled Ovens by Gallenkamp. These will be used for drying filter papers for suspended solids.
- (4) Mettler electronic balance capable of weighing to five decimal places.
- (5) Certified Class A grade volumetric glassware will be used.

4:4 Calibration:

A programme of regular service by an outside agency is in place for the maintenance of the Atomic Absorption Spectrometer and the Balance. This service is performed annually. In addition, daily checks are maintained of the

- (a) photomultiplier volts and the
- (b) expected absorbance of standards for the Atomic Absorption Spectrometer.

(c) daily check weight for the balance.

Standards for calibration will be prepared from certified stock solutions using grade A volumetric glassware and stored in polyethylene containers.

The Atomic Absorption instrument will be calibrated before each batch run and a check standard and blank will be run after every ten samples.

The pH meter will be calibrated daily using certified Buffers. The slope will be recorded in the pH meter log book. A temperature compensator probe will be used to take account of variable temperature of samples.

4:4.1 Intra laboratory control

The laboratory has an intra laboratory quality control (Q.C) system in place, whereby a quality control sample is read with each batch and the value plotted on the Q.C chart. (see example). Warning limits and control limits are set and appropriate action will be taken if the result is outside these limits. The Q.C sample is prepared from stock other than the stock from which the calibration standards are made.

4:4.2 Proficiency testing

The laboratory is not involved in external proficiency testing (P.T.) for water samples at present. The benefits of Proficiency Testing were discussed in Section 3:4.6.2. It is recommended that the laboratory become a contributor to an external P.T scheme such as Aquacheck U.K. This would provide an independent and objective means of assessing and confirming the continuing reliability of laboratory data.

4:5 Test methods and procedures:

In general, methods which are accepted and taken as standard or national methods shall be used. Test methods and procedures for each test will be documented and available to workers at all times. The test methods and procedures will be collected in a "Methods Manual".

For the chosen tests within the scope of accreditation, the following methods will be used;

4:5.1 pH measurement

Refer to the manufacturers instructions for calibration of the pH meter. The method of measurement in Standard Methods for the examination of water and wastewater (1989 17th edition) will be used. The test should be carried out as soon as possible but may be held for six hours before analysis. (BS 6068: section 6.3: 1986)

4:5.2 Suspended solids

The British Standard method BS 2690:Part 120:1981 will be used for analysis of suspended solids. No modifications to the method are required.

4:5.3 Zinc and Lead determination

The concentration of dissolved metals is required on process waters. On arrival at the laboratory, the sample will be filtered through a 0.45 um filter paper and stored in a polyethylene bottle. An aliquot will then be fixed with Foodstuff grade certified Nitric Acid to attain a pH of <2. Samples thus fixed may be stored for a period of one month without particular difficulty. (BS 6068: section 6.3:1986).

The British Standard Method BS 6068: Section 2.29:1987 will be used. Section one, Method A- Direct determination by flame atomic absorption spectrometry applies to the type of samples in this case.

Refer to the manufacturers instructions for setting up the instrument.

Use of the Atom Concentrator Tube (A.C.T) will give an increase in the absorbance detected in determining Lead. The background correction system will also be used for Lead determination. Zinc determination does not require use of background correction or A.C.T.

4:6 Environment

The physical features within the laboratory will be such, so as to provide

1. a proper environment for optimum operation of equipment and instrumentation
2. a proper environment for optimum performance of employees.

Access to the Environmental laboratory will be restricted to designated personnel only. This is to ensure that;

- A. test items cannot be lost or damaged
- B. equipment is reasonably protected from accidental damage
- C. client confidentiality is not prejudiced
- D. interference by contamination is minimised

Because the Environmental laboratory is contained within the main laboratory building, a simple locking system will be introduced for security reasons. This could be in the form of a number coded lock on the laboratory door, so that only personnel with the correct code can gain entry.

A sign in system for visitors will also be set up to accommodate people who may need to visit the laboratory from time to time (e.g. service technicians, maintenance personnel, cleaning staff.)

Windows will remain closed to avoid contamination from dust and fumes. An adequate air conditioning system must therefore be installed to allow for control of temperature. Delicate equipment (e.g. balance) will be protected from vibration.

4:7 Handling of items to be tested:

Samples must be handled in such a way as to avoid mix-up and maintain the sample in a correct state before and during analysis.

Samples are delivered to the laboratory by hand or arrive by internal post. Samples are accompanied by an assay requisition sheet. A computerised system is installed in the laboratory and each sample is logged in to the electronic system on receipt. The computer generates a unique laboratory identification number for each sample entered. This laboratory number is prefixed by a letter indicating the type of sample. This laboratory identification is used on all data pertaining to that particular sample.

For Example;

<u>Waters</u>	labelled W1	up to	W1000 then
	WA1	up to	WA1000 etc.
<u>Dusts</u>	labelled D1	up to	D1000 then
	DA1	up to	DA1000 etc.

Samples will be stored according to the instructions on the test methods.

The use of pre printed log in sheets should be considered. This sheet will contain all the information necessary to identify the sample including comments on the condition

of the sample on arrival. This "chain of custody" form should be signed by the client and by the technician receiving the sample. (see sample chain of custody form).

Refrigerate samples where appropriate.

4:8 Records:

Records of all primary data relating to tests performed will be maintained by the laboratory. Records will be stored in accordance with the procedures set out in the Quality Manual.

4:8.1 pH records

pH equipment log will be kept up to date. The slope will be recorded daily. pH results will be recorded in a hard covered notebook and all notebooks will be signed and dated by the operator.

4:8.2 Suspended solids

Pre printed worksheets are provided for storage of primary data relating to suspended solids. (see sample worksheet). The balance check weight reading will be recorded daily in a log book.

4:8.3 Metals determinations;

Records of instrument photomultiplier volts will be recorded daily on a chart. All printouts from the A.A will be clearly marked with any dilutions which were made. Preparation of standards will be recorded in the "Standards Notebook". All notebooks will be signed and dated. Quality Control check results will be recorded on Q.C charts.

All records will be held in the main office and be easily obtainable.

4:9 Test Reports:

When a sample is completed, the results are entered into the computer system. These results are then checked and approved by the Chief Chemist or in his absence, the Laboratory Supervisor. A test report is then printed out and sent to the client.

4:10 Complaints:

A complaints notebook will be maintained in the laboratory by the Quality manager. Any queries, comments, or complaints relating to samples received will be recorded and investigated. Where necessary a corrective action will be employed and the client notified as soon as possible.

CHAPTER FIVE

**MAINTENANCE AND IMPLEMENTATION OF AN
ACCREDITATION SYSTEM AT
TARA MINES ENVIRONMENTAL LABORATORY**

5:0 Maintenance and Implementation of accreditation system at Tara Mines Environmental Laboratory.

Once a system of accreditation is in place, and up and running, it is necessary to periodically review and examine the system to be sure that the programme is continually being implemented.

Such reviews and examinations are called **Audits**, and there are several different types.

Internal Audits are those performed by the laboratory itself or its parent organisation.

External Audits are those carried out by an external organisation, such as an accrediting body.

The Audit programme, should provide for both **Horizontal and Vertical Audits**.

A Horizontal Audit involves a detailed check on one or more elements of the quality system, such as staff training, testing and measuring equipment, quality control activities or test methods.

In a Vertical Audit, a representative number of performed tests are selected at random from work that has recently passed through the laboratory. The vertical audit should include, where possible, the repetition of the test involved.

Each aspect of the laboratory's activities associated with the selected tests should be checked including;

- sample handling and identification;
- staff involved;
- calibration and maintenance of equipment;
- test methods and procedures used;
- quality control requirements;
- environmental conditions during testing;

- test records and the reporting of results;
- storage of data.

Internal audits are at the heart of an accredited quality system. These need to become ongoing and completely integrated into the operation of the laboratory. (Kibblewhite, 1993). An accredited laboratory should carry out internal quality audits at regular intervals to ensure that its quality system is fully implemented in practice. In these audits it should be checked whether or not the requirements stated in the laboratory's quality manual and related documents are applied at all levels of work. The non-compliances found at internal quality audits give valuable information for the improvement of the laboratory's quality system. (Anon.WELAC 1993)

External Audits on the other hand, are carried out by an outside organisation such as an accrediting body.

The purpose being to qualify the laboratory for accreditation by the auditing agency.

5:1 Reasons for Auditing:

A programme of periodic audits must be planned to establish that;

1. Management objectives are met in all respects.
2. Assigned personnel are satisfactorily carrying out their duties and responsibilities.
3. Methods of operation are in accordance with the policies in the Quality Manual.
4. The requirements of the accrediting body are met on a continuing basis.
5. To instil in staff a sense of pride and confidence in the quality of their work and the results produced.

(ILAB Quality Audits)

Audits are designed to reveal defects or irregularities in all of the elements examined and serve to check on the abilities and integrity of Laboratory Management's at all levels. To assist in the auditing process, audit checklists may be used. These can be amended, in light of experience gained from the audit itself, or any complaints received. For each item found not to be in compliance with the procedures in the Quality Manual, or with criteria set by the accrediting body, a Non-Compliance Report is completed by the auditor. A corrective action and a timetable for its completion is decided by the Quality Manager and implemented.

5:2 Examination of the Quality System:

Each month, some aspect of the Quality System must be examined in detail, so that all aspects are examined at least once a year.

For example;

1. Organisation

This will include; The Quality Manual itself, amendment procedures, Laboratory Documentation, Laboratory notebooks, test reports.

2. Staff

Training, Training records, competence, performance in any round robin tests or with control tests.

3. Testing and Measuring Equipment

Suitability, maintenance, records, approved vendors list.

4. Calibration

Traceability, documentation in date for all measuring equipment in use.

5. Test Methods and Procedures

All tests being carried out exactly to the stated methods or procedures, all records being maintained and initialled, all methods used up to date, all necessary equipment for the tests available and in service. The performance of actual tests observed.

6. Environment

Check that it does not invalidate any test results. Security of the data, adequate cleaning and housekeeping. Records of tests of environmental conditions, adequacy of air filters.

7. Handling of Items to be Tested

Samples correctly labelled, retained in correct conditions, sample containers clean and suitable.

8. Records

All required files are maintained up to date and for the required periods. All records of observations and calculations made in the required notebooks at the time they are made. All records contain sufficient information to permit satisfactory repetition of the test under original conditions.

9. Control Samples

Suitable, stable, used with frequency specified in the procedures, all trends and irregularities indicated by their use investigated, and the appropriate corrective action taken.

10. Complaints

All complaints recorded and investigated, corrective action determined, implemented and follow up audit carried out in accordance with procedures.

Non-compliances found as a result of an audit should be recorded and the appropriate corrective action and time limit for correction agreed. A complete record of the audit should be maintained even where no non-compliances have been found. All records

of audits should be stored for an agreed period of time. An example of an Audit checklist is provided in Figure 5.1.

5:3 Implementation of system:

A schedule for implementation of an accreditation system is given in the following table. The time scale chosen is over one year. (Figure 5.2)

Figure 5.1 AUDIT CHECKLIST

Tara Mines Environmental Laboratory.												
Aspect to be Audited.	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Organization			■									
Staff					■							
Testing & Measuring Equipment							■					
Calibration	■			■			■			■		
Test Methods and Procedures									■			
Environment			■			■			■			■
Handling of Items to be Tested											■	
Records	■											
Control Samples				■								
Complaints						■						
Test reports		■			■			■			■	

Figure 5.2

IMPLEMENTATION SCHEDULE

TASK	SYSTEM		SETUP				MAINTAIN & DEMONSTRATE COMPLIANCE			
	JUNE	JULY	AUG	SEPT	OCT	NOV	DEC	JAN '96	FEB '96	MAR '96
Launch of project, inform personnel.	→									
Staff organization.	→									
Establish scope & examine methods.			→							
Amend Quality Manual Prepare worksheets.	-----→									
Establish proficiency testing scheme.		-----→								
Equipment & environment :										
Security system										
Air conditioning		→								
Visitor log in										
Sample log in procedures.	→									

CHAPTER SIX

CONCLUSIONS

6:0 Conclusions:

- (1) This study has clearly identified the requirements for a laboratory accreditation system through literature research.
- (2) Accreditation by the National Accreditation Board provides the most suitable system for the laboratory at Tara Mines.
- (3) Tara Mines Laboratory can, with management commitment, achieve a limited scope accreditation within a year using the schedule proposed in this study.

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P2; *Regulations for ILAB accredited laboratories.*

P3; *Guide to the interpretation of ILAB publications P1 and P2.*

P4; *Guidance notes for the compilation of a Quality Manual for a testing laboratory.*

P5; *Guide to the calibration of equipment for ILAB accredited laboratories.*

P6; *Guide to the preparation of an application for ILAB accreditation.*

P7; *Guide to ILAB assessment procedures for laboratories.*

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APPENDICES

APPENDIX A; SAMPLE PMV WORKSHEET

AAS 01

Varian Atomic Absorption Spectrometer AA 300 - (Furnace) GTA

Date: _____

Photomultiplier Voltage Daily Records

Element	Date pmv	Date pmv	Date pmv	Date pmv	Date pmv	Date pmv	Date pmv	Date pmv	Date pmv	Date pmv	Date pmv	Date pmv	Date pmv	Date pmv	Date pmv	Date pmv	Date pmv	Date pmv	Date pmv	Date pmv	Date pmv	Date pmv	
Zn																							
Pb																							
Cu																							
Fe																							
Cr																							
Sb																							
Cd																							

NOTES:

APPENDIX B;
 SAMPLE SUSPENDED SOLIDS WORKSHEET



outokumpu zinc
 TARA MINES

SSWS 006

LABORATORY WORKSHEET

Suspended Solids / Sulphate / Total Dissolved Solids

Balance No: _____

Date Weighed: _____

Sample No.	Lab No.	Date / Analyst	Analysis	Volume	Code No.	Initial Weight	Final Weight	Factor	Results	Remarks

LABORATORY

SAMPLE RECEPTION FORM

Client: _____ Your Ref./Order No.: _____
Address: _____
Our Ref./Quotation No.: _____
Tel. No: _____ Fax No: _____
Contact Name: _____ Your Laboratories
Contact Name: _____

Type of Samples: _____
(Please use separate form for each type of sample/matrix)
Number of Samples _____
Your I.D. of Samples _____
Date of Sampling: _____ Samples collected by: _____

Type of Analysis Required: (Please be as specific as possible) _____

Recommended Storage Conditions: _____

Date: _____ Name (Block Letters) _____ Signature: _____

(To be completed by Laboratories Staff)

Samples Received by: _____

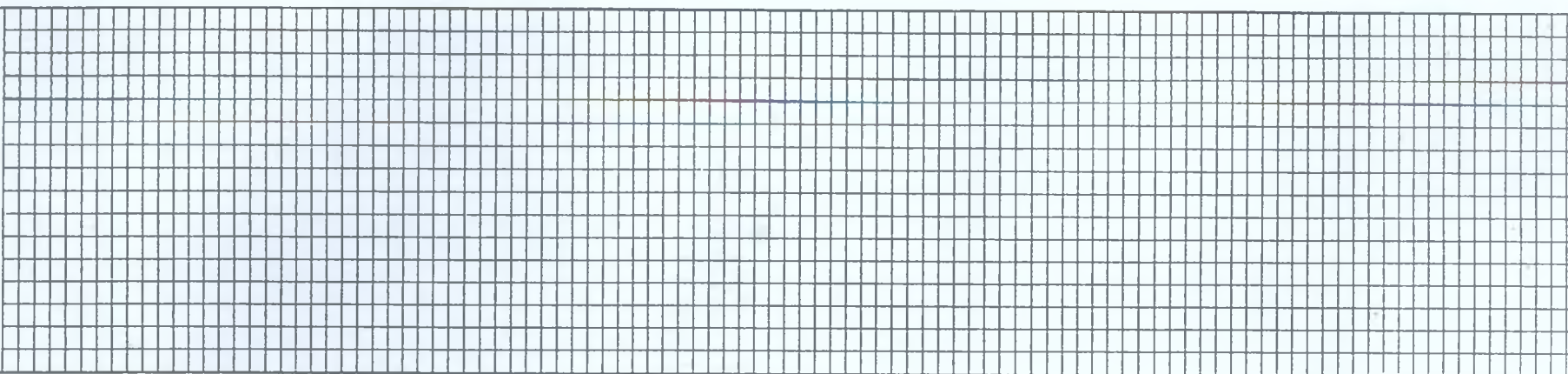
Remarks: _____

Date: _____ Signature: _____



TARA MINES LTD. ENVIRONMENTAL LABORATORIES

Q.C. Form No : Control sample/CRM ref. No: Scientist 1:..... Syntol:..... Scientist 2:..... Syntol:.....

SAMPLE AVERAGES N =																														
---------------------------	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

SAMPLE RANGES N =																														
-------------------------	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

Data 1																																			
Data 2																																			
Data 3																																			
Data 4																																			
Data 5																																			
Data 6																																			

Total																																			
Average																																			
Range																																			
Difference																																			
Date																																			
Scientist																																			

4500-H⁺ pH VALUE*

4500-H⁺ A. Introduction

1. Principles

Measurement of pH is one of the most important and frequently used tests in water chemistry. Practically every phase of water supply and wastewater treatment, e.g., acid-base neutralization, water softening, precipitation, coagulation, disinfection, and corrosion control, is pH-dependent. pH is used in alkalinity and carbon dioxide measurements and many other acid-base equilibria. At a given temperature the intensity of the acidic or basic character of a solution is indicated by pH or hydrogen ion activity. Alkalinity and acidity are the acid- and base-neutralizing capacities of a water and usually are expressed as milligrams CaCO₃ per liter. Buffer capacity is the amount of strong acid or base, usually expressed in moles per liter, needed to change the pH value of a 1-L sample by 1 unit. pH as defined by Sorenson¹ is $-\log [H^+]$; it is the "intensity" factor of acidity. Pure water is very slightly ionized and at equilibrium the ion product

$$[H^+][OH^-] = K_w \\ = 1.01 \times 10^{-14} \text{ at } 25^\circ\text{C} \quad (1)$$

and

$$[H^+] = [OH^-] \\ = 1.005 \times 10^{-7}$$

where:

$[H^+]$ = activity of hydrogen ions, moles/L,
 $[OH^-]$ = activity of hydroxyl ions, moles/L, and
 K_w = ion product of water.

Because of ionic interactions in all but very dilute solutions, it is necessary to use activity rather than concentration and not its molar

concentration. Use of the term pH assumes that the activity of the hydrogen ion, a_{H^+} , is being considered. The approximate equivalence to molarity, $[H^+]$ can be presumed only in very dilute solutions (ionic strength < 0.1).

A logarithmic scale is convenient for expressing a wide range of ionic activities. Equation 1 in logarithmic form and corrected to reflect activity is:

$$(-\log_{10} a_{H^+}) + (-\log_{10} a_{OH^-}) = 14 \quad (2)$$

or

$$pH + pOH = pK_w$$

where:

$$pH \dagger = -\log_{10} a_{H^+} \text{ and} \\ pOH = -\log_{10} a_{OH^-}.$$

Equation 2 states that as pH increases pOH decreases correspondingly and vice versa because pK_w is constant for a given temperature. At 25°C, pH 7.0 is neutral, the activities of the hydrogen and hydroxyl ions are equal, and each corresponds to an approximate activity of 10^{-7} moles/L. The neutral point is temperature-dependent and is pH 7.5 at 0°C and pH 6.5 at 60°C.

The pH value of a highly dilute solution is approximately the same as the negative common logarithm of the hydrogen ion concentration. Natural waters usually have pH values in the range of 4 to 9, and most are slightly basic because of the presence of bicarbonates and carbonates of the alkali and alkaline earth metals.

2. Reference

1. SORENSON, S. 1909. Über die Messung und die Bedeutung der Wasserstoff Ionen Konzentration bei Enzymatischen Prozessen. *Biochem. Z.* 21: 131.

4500-H⁺ B. Electrometric Method

1. General Discussion

a. Principle: The basic principle of electrometric pH measurement is determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode and a reference electrode. The hydrogen electrode consists of a platinum electrode across which hydrogen gas is bubbled at a pressure of 101 kPa. Because of difficulty in its use and the potential for poisoning the hydrogen electrode, the glass electrode commonly is used. The electromotive force (emf) produced in the glass electrode system varies linearly with pH. This linear relationship is described by plotting the measured emf against the pH of different buffers. Sample pH is determined by extrapolation.

Because single ion activities such as a_{H^+} cannot be measured, pH is defined operationally on a potentiometric scale. The pH measuring instrument is calibrated potentiometrically with an indicating (glass) electrode and a reference electrode using National Institute of Standards and Technology (NIST, formerly National Bureau of Standards) buffers having assigned values so that:

$$pH_s = -\log_{10} a_{H^+}$$

where:

$$pH_s = \text{assigned pH of NIST buffer.}$$

The operational pH scale is used to measure sample pH and is defined as:

$$pH_s = pH_x \doteq \frac{F(E_s - E_x)}{2.303 RT}$$

where:

$$pH_s = \text{potentiometrically measured sample pH.}$$

- F = Faraday: 9.649×10^4 coulomb/mole.
- E_s = sample emf, V,
- E_x = buffer emf, V,
- R = gas constant: 8.314 joule/(mole · °K), and
- T = absolute temperature, °K.

NOTE: Although the equation for pH_s appears in the literature with a plus sign, the sign of emf readings in millivolts for most pH meters manufactured in the U.S. is negative. The choice of negative sign is consistent with the IUPAC Stockholm convention concerning the sign of electrode potential.^{1,2}

The activity scale gives values that are higher than those on Sorenson's scale by 0.04 units:

$$pH (\text{activity}) = pH (\text{Sorenson}) + 0.04$$

The equation for pH_s assumes that the emf of the cells containing the sample and buffer is due solely to hydrogen ion activity unaffected by sample composition. In practice, samples will have varying ionic species and ionic strengths, both affecting H^+ activity. This imposes an experimental limitation on pH measurement; thus, to obtain meaningful results, the differences between E_s and E_x should be minimal. Samples must be dilute aqueous solutions of simple solutes (< 0.2M). (Choose buffers to bracket the sample.) Determination of pH cannot be made accurately in nonaqueous media, suspensions, colloids, or high-ionic strength solutions.

b. Interferences: The glass electrode relatively free from interference from turbidity, colloidal matter, oxidants, ductants, or high salinity, except for a small error at pH > 10. Reduce this error by using special "low sodium error" electrodes.

pH measurements are affected by temperature in two ways: mechanical and



that are caused by changes in the properties of the electrodes and chemical effects caused by equilibrium changes. In the first instance, the Nernstian slope increases with increasing temperature and electrodes take time to achieve thermal equilibrium. This can cause long-term drift in pH. Because chemical equilibrium affects pH, standard pH buffers have a specified pH at indicated temperatures.

Always report temperature at which pH is measured.

2. Apparatus

a. pH meter consisting of potentiometer, a glass electrode, a reference electrode, and a temperature-compensating device. A circuit is completed through the potentiometer when the electrodes are immersed in the test solution. Many pH meters are capable of reading pH or millivolts and some have scale expansion that permits reading to 0.001 pH unit, but most instruments are not that precise.

For routine work use a pH meter accurate and reproducible to 0.1 pH unit with a range of 0 to 14 and equipped with a temperature-compensation adjustment.

Although manufacturers provide oper-

ating instructions, the use of different descriptive terms may be confusing. For most instruments, there are two controls: intercept (set buffer, asymmetry, standardize) and slope (temperature, offset); their functions are shown diagrammatically in Figures 4500-H⁺:1 and 2. The intercept control shifts the response curve laterally to pass through the isopotential point with no change in slope. This permits bringing the instrument on scale (0 mV) with a pH 7 buffer that has no change in potential with temperature.

The slope control rotates the emf/pH slope about the isopotential point (0 mV/pH 7). To adjust slope for temperature without disturbing the intercept, select a buffer that brackets the sample with pH 7 buffer and adjust slope control to pH of this buffer. The instrument will indicate correct millivolt change per unit pH at the test temperature.

b. Reference electrode consisting of a half cell that provides a constant electrode potential. Commonly used are calomel and silver: silver-chloride electrodes. Either is available with several types of liquid junctions.

The liquid junction of the reference electrode is critical because at this point the

electrode forms a salt bridge with the sample or buffer and a liquid junction potential is generated that in turn affects the potential produced by the reference electrode. Reference electrode junctions may be annular ceramic, quartz, or asbestos fiber, or the sleeve type. The quartz type is most widely used. The asbestos fiber type is not recommended for strongly basic solutions. Follow the manufacturer's recommendation on use and care of the reference electrode.

Refill nonsealed electrodes with the correct electrolyte to proper level and make sure junction is properly wetted.

c. Glass electrode: The sensor electrode is a bulb of special glass containing a fixed concentration of HCl or a buffered chloride solution in contact with an internal reference electrode. Upon immersion of a new electrode in a solution the outer bulb surface becomes hydrated and exchanges sodium ions for hydrogen ions to build up a surface layer of hydrogen ions. This, together with the repulsion of anions by fixed, negatively charged silicate sites, produces at the glass-solution interface a potential that is a function of hydrogen ion activity in solution.

Several types of glass electrodes are available. Combination electrodes incorporate the glass and reference electrodes into a single probe. Use a "low sodium error" electrode that can operate at high temperatures for measuring pH over 10 because standard glass electrodes yield erroneously low values. For measuring pH below 1 standard glass electrodes yield erroneously high values; use liquid membrane electrodes instead.

d. Beakers: Preferably use polyethylene or TFE* beakers.

e. Stirrer: Use either a magnetic, TFE-coated stirring bar or a mechanical stirrer with inert plastic-coated impeller.

f. Flow chamber: Use for continuous flow measurements or for poorly buffered solutions.

3. Reagents

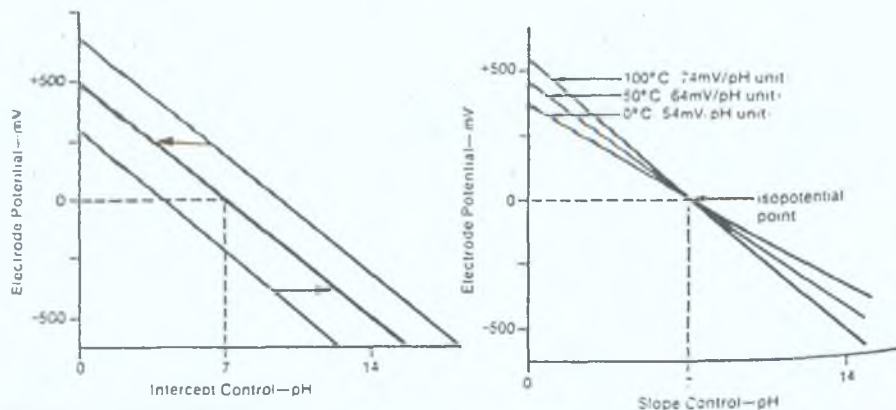
a. General preparation: Calibrate the electrode system against standard buffer solutions of known pH. Because buffer solutions may deteriorate as a result of mold growth or contamination, prepare fresh as needed for accurate work by weighing the amounts of chemicals specified in Table 4500-H⁺:I, dissolving in distilled water at 25°C, and diluting to 1000 mL. This is particularly important for borate and carbonate buffers.

Boil and cool distilled water having a conductivity of less than 2 $\mu\text{mhos/cm}$. To 50 mL add 1 drop of saturated KCl solution suitable for reference electrode use. If the pH of this test solution is between 6.0 and 7.0, use it to prepare all standard solutions.

Dry KH_2PO_4 at 110 to 130°C for 2 h before weighing but do not heat unstable hydrated potassium tetroxalate above 60°C nor dry the other specified buffer salts.

Although ACS-grade chemicals generally are satisfactory for preparing buffer solutions, use certified materials available from the National Institute of Standards and Technology when the greatest accuracy is required. For routine analysis, use commercially available buffer tablets, powders, or solutions of tested quality. In preparing buffer solutions from solid salts, insure complete solution.

As a rule, select and prepare buffer solutions classed as primary standards in Table 4500-H⁺:I; reserve secondary standards for extreme situations encountered in wastewater measurements. Consult Table 4500-H⁺:II for accepted pH of standard buffer solutions at temperatures other than 25°C. In routine use, store buffer solutions



b. Saturated potassium hydrogen tartrate solution: Shake vigorously an excess (5 to 6) of finely crystalline $\text{KHC}_4\text{H}_4\text{O}_6$ with 1 to 500 mL distilled water at 25°C in a stoppered bottle. Separate clear solution from undissolved material by decantation or filtration. Preserve for 2 months more by adding one thymol crystal (8 mm diam) per 200 mL solution.

c. Saturated calcium hydroxide solution: Obtain a well-washed, low-alkali grade CaCO_3 in a platinum dish by igniting for 1 h at 1000°C. Cool, hydrate by slowly adding distilled water with stirring, and heat to boiling. Cool, filter, and collect solid Ca(OH)_2 on a fritted glass filter of medium porosity. Dry at 110°C, cool, and pulverize to uniformly fine granules. Vigorously shake an excess of fine granules with distilled water in a stoppered polyethylene bottle. Let temperature come to 25°C after mixing. Filter supernatant under suction through a sintered glass filter of medium porosity and use filtrate as the buffer solution. Discard buffer solution when atmospheric CO_2 causes turbidity to appear.

d. Auxiliary solutions: 0.1N NaOH, 0.1N HCL, 0.1N HCl (dilute five volumes 6N HCl with one volume distilled water), and acid potassium fluoride solution (dissolve 2 g KF in 2 mL conc H_2SO_4 and dilute to 100 mL with distilled water).

4. Procedure

a. Instrument calibration: In each case follow manufacturer's instructions for pH meter and for storage and preparation of electrodes for use. Recommended solutions for short-term storage of electrodes vary with type of electrode and manufacturer, but generally have a conductivity greater than 100 $\mu\text{S/cm}$. Tap water is a better

wet by returning them to storage solution whenever pH meter is not in use.

Before use, remove electrodes from storage solution, rinse, blot dry with a soft tissue, place in initial buffer solution, and set the isopotential point (see 2a above). Select a second buffer within 2 pH units of sample pH and bring sample and buffer to same temperature, which may be the room temperature, a fixed temperature such as 25°C, or the temperature of a fresh sample. Remove electrodes from first buffer, rinse thoroughly with distilled water, blot dry, and immerse in second buffer. Record temperature of measurement and adjust temperature dial on meter so that meter indicates pH value of buffer at test temperature (this is a slope adjustment).

Use the pH value listed in the tables for the buffer used at the test temperature. Remove electrodes from second buffer, rinse thoroughly with distilled water and dry electrodes as indicated above. Immerse in a third buffer below pH 10, approximately 3 pH units different from the second; the reading should be within 0.1 unit for the pH of the third buffer. If the meter response shows a difference greater than 0.1 pH unit from expected value, look for trouble with the electrodes or potentiometer (see 5a and b below).

The purpose of standardization is to adjust the response of the glass electrode to the instrument. When only occasional pH measurements are made standardize instrument before each measurement. When frequent measurements are made and the instrument is stable, standardize less frequently. If sample pH values vary widely, standardize for each sample with a buffer having a pH within 1 to 2 pH units of the sample.

b. Sample measurement: Establish equilibrium

ing by dipping them into sample for 1 min. Blot dry, immerse in a fresh portion of the same sample, and read pH.

With dilute, poorly buffered solutions, equilibrate electrodes by immersing in three or four successive portions of sample. Take a fresh sample to measure pH.

5. Trouble Shooting

a. Potentiometer: To locate trouble source disconnect electrodes and, using a short-circuit strap, connect reference electrode terminal to glass electrode terminal. Observe change in pH when instrument calibration knob is adjusted. If potentiometer is operating properly, it will respond rapidly and evenly to changes in calibration over a wide scale range. A faulty potentiometer will fail to respond, will react erratically, or will show a drift upon adjustment. Switch to the millivolt scale on which the meter should read zero. If inexperienced, do not attempt potentiometer repair other than maintenance as described in instrument manual.

b. Electrodes: If potentiometer is functioning properly, look for the instrument fault in the electrode pair. Substitute one electrode at a time and cross-check with two buffers that are about 4 pH units apart. A deviation greater than 0.1 pH unit indicates a faulty electrode. Glass electrodes fail because of scratches, deterioration, or accumulation of debris on the glass surface. Rejuvenate electrode by alternately immersing it three times each in 0.1N HCl and 0.1N NaOH. If this fails, immerse tip in KF solution for 30 s. After rejuvenation, soak in pH 7.0 buffer overnight. Rinse and store in pH 7.0 buffer. Rinse again with distilled water before use. Protein coatings can be removed by soaking glass electrodes in a 10% pepsin solution adjusted to pH

plug good reference electrode into glass electrode jack of potentiometer; then plug questioned electrode into reference electrode jack. Set meter to read millivolts and take readings with both electrodes immersed in the same electrolyte (KCl) solution and then in the same buffer solution. The millivolt readings should be 0 ± 5 mV for both solutions. If different electrodes are used, i.e., silver: silver-chloride against calomel or vice versa, the reading will be 44 ± 5 mV for a good reference electrode.

Reference electrode troubles generally are traceable to a clogged junction. Interruption of the continuous trickle of electrolyte through the junction causes increase in response time and drift in reading. Clear a clogged junction by applying suction to the tip or by boiling tip in distilled water until the electrolyte flows freely when suction is applied to tip or pressure is applied to the fill hole. Replaceable junctions are available commercially.

6. Precision and Bias

By careful use of a laboratory pH meter with good electrodes, a precision of ± 0.02 pH unit and an accuracy of ± 0.05 pH unit can be achieved. However, ± 0.1 pH unit represents the limit of accuracy under normal conditions, especially for measurement of water and poorly buffered solutions. For this reason, report pH values to the nearest 0.1 pH unit. A synthetic sample of a Clark and Lubs buffer solution of pH 7.3 was analyzed electrometrically by 30 laboratories with a standard deviation of ± 0.13 pH unit.

7. References

1. BATES, R.G. 1978. Concept and determination of pH. In I.M. Kolthoff & P.J. Elving, eds. *Treatise on Analytical Chemistry*. Part 1, Vol.



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British Standard

Water quality

Part 2. Physical, chemical and biochemical methods

Section 2.29 Determination of cobalt, nickel, copper, zinc, cadmium and lead: flame atomic absorption spectrometric methods

[ISO title: Water quality – Determination of cobalt, nickel, copper, zinc, cadmium and lead – Flame atomic absorption spectrometric methods]

Qualité de l'eau

Partie 2. Méthodes physiques, chimiques et biochimiques

Section 2.29 Dosage du cobalt, du nickel, du cuivre, du zinc, du cadmium et du plomb:
méthode par spectrométrie d'absorption atomique à la flamme

Wasserqualität

Teil 2. Physikalische, chemische und biochemische Verfahren

Abschnitt 2.29 Bestimmung von Kobalt, Nickel, Kupfer, Zink, Kadmium und Blei
mittels Flammenatomabsorptionsspektrometrie

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National foreword

This Section of BS 6068, which has been prepared under the direction of the Environment and Pollution Standards Committee, is identical with ISO 8288-1986 'Water quality — Determination of cobalt, nickel, copper, zinc, cadmium and lead — Flame atomic absorption spectrometric methods'. The international standard was prepared by subcommittee 2, Physical, chemical and biochemical methods, of Technical Committee 147, Water quality, of the International Organization for Standardization (ISO) as a result of discussion in which the UK participated.

This British Standard is being published in a series of Parts subdivided into Sections that will generally correspond to particular international standards. Sections are being, or will be, published in Parts 1 to 6, which together with Part 0, are listed below.

- Part 0. Introduction
- Part 1. Glossary
- Part 2. Physical, chemical and biochemical methods
- Part 3. Radiological methods
- Part 4. Microbiological methods
- Part 5. Biological methods
- Part 6. Sampling

Terminology and conventions. The text of the international standard has been approved as suitable for publication as a British Standard without deviation. Some terminology and certain conventions are not identical with those used in British Standards; attention is drawn especially to the following.

The comma has been used as a decimal marker. In British Standards it is current practice to use a full point on the baseline as the decimal marker.

In British Standards it is current practice to use the symbol 'L' for litre (and in its submultiples) rather than 'l', and to use the spelling 'sulphur', etc., instead of 'sulfur', etc.

Wherever the words 'this International Standard' appear, referring to this standard, they should be read as 'this Section of this British Standard'.

NOTE. *Typographical errors.* In 18.6, paragraph 1, line 1, and paragraph 3, line 1, 'solutions' should be read as 'solution'.

In 22.3, paragraph 3, line 1, 'neutral' should be read as 'natural'.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Scope

International Standard specifies three methods for the determination of cobalt, nickel, copper, zinc, cadmium and lead in water by flame atomic absorption spectrometry:

Section one: method A, for direct determination by flame atomic absorption spectrometry; ✓

Section two: method B, for determination by flame atomic absorption spectrometry after chelation (APDC) and extraction (MIBK);

Section three: method C, for determination by flame atomic absorption spectrometry after chelation (HMA-MDC) and extraction (DIPK-xylene).

Field of application

Method A is particularly applicable when concentrations of elements to be analysed are relatively high and when there are no interferences.

If the samples are of a complex or unknown nature or if they contain high concentrations of dissolved solids (e.g. in sea or brackish waters) method A is not applicable and method B or C should be selected.

The concentrations of elements which can be determined by method A may vary according to the characteristics of the atomic absorption spectrometric apparatus used but are generally in the ranges indicated in table 1.

Table 1

Element to be determined	Range of determination (mg/l)
Cobalt	0,1 to 10
Nickel	0,1 to 10
Copper	0,05 to 6
Zinc	0,05 to 2
Cadmium	0,02 to 2
Lead	0,2 to 10

If concentrations are greater than the upper limits indicated in table 1, the sample may be diluted before analysis.

Methods B and C are applicable when concentrations of elements to be analysed in the sample (or dilution of the sample) are greater than 0,5 µg/l.

2.2.1 Method B

The concentrations of the elements which can be determined by method B may vary according to the characteristics of the atomic absorption spectrometer used but are generally in the ranges indicated in table 2.

Table 2

Element to be determined	Range of determination (µg/l)
Cobalt	1 to 200
Nickel	1 to 200
Copper	1 to 200
Zinc	0,5 to 50
Cadmium	0,5 to 50
Lead	5 to 200

2.2.2 Method C

With a ratio of test portion to extraction solution of 20 to 1 by volume as indicated in 21.2, the concentrations of elements which can be determined by method C vary as indicated in table 3.

Table 3

Element to be determined	Range of determination (µg/l)
Cobalt	0,5 to 100
Nickel	0,5 to 100
Copper	0,5 to 100
Zinc	0,2 to 50
Cadmium	0,2 to 50
Lead	2 to 200

Lower concentrations may be determined by choosing a higher ratio of test portion to extraction solution. A ratio of 50 to 1 by volume is possible since the organic solvent mixture is only very slightly soluble in water.

With method C, separation of the aqueous and the organic phases is faster. The metal chelates, especially the Cd-chelate, are more stable in the organic solvent mixture.

NOTES

1 When determining total metals, it is necessary to pretreat the sample before analysis (see examples of procedures in annex A).

2 Methods B and C are not applicable when the chemical oxygen demand (COD) of the samples (or diluted samples) is greater than 500 mg/l.

Section one: Method A — Direct determination by flame atomic absorption spectrometry

3 Principle

Aspiration into the flame of an atomic absorption spectrometer of a test portion of the acidified filtrate of the sample (or diluted sample).

Direct determination of the concentration of each element, either from the specific absorbance of each element using a spectrometer fitted with a continuous background correction system, or, in the absence of such a system, after having carried out a correction for a non-specific absorbance.

4 Reagents

All reagents shall be of recognized analytical grade so that their use does not affect the accuracy of the determination. The water used shall be deionized water or distilled water containing no detectable concentration of the metals being determined when analysed by a blank test.

4.1 Nitric acid, $\rho = 1,4$ g/ml.

4.2 Nitric acid, $c(\text{HNO}_3) \approx 1,5$ mol/l.

Add 100 ml of nitric acid (4.1) to 600 ml of water and dilute to 1 000 ml.

4.3 Nitric acid, $c(\text{HNO}_3) \approx 0,03$ mol/l.

Add 1 ml of nitric acid (4.1) to 400 ml of water and dilute to 500 ml with water.

4.4 Metals, standard solutions corresponding to 1,000 g of metal per litre.¹⁾

For each element to be determined, weigh 1,000 g of pure metal and dissolve it in nitric acid (4.1), heating to effect complete dissolution. Allow to cool and transfer each solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

For preparing standard solutions, it is also permissible to use metal salts of accurately known composition.

Store each of the standard solutions in either polyethylene or borosilicate glass containers.

1 ml of each of these standard solutions contains 1,00 mg of the respective metal.

5 Apparatus

Usual laboratory equipment, and

Atomic absorption spectrometer, fitted with hollow cathode lamps for the appropriate metals or electrodeless

discharge lamps, and with a suitable device for allowing for the correction of the non-specific absorbance and with a nebulizer-burner with an acetylene-air flame.

Follow the manufacturer's instructions for adjusting all instrument parameters.

NOTE ON CLEANING OF GLASSWARE

All the glassware shall be carefully soaked in nitric acid (4.2) then rinsed with water.

6 Sampling and samples

6.1 Polyethylene or borosilicate glass containers which have been previously cleaned with nitric acid (4.2) then rinsed with water, shall be used for sampling.

6.2 If total metals are to be determined, samples shall be treated by the addition of nitric acid (4.1) immediately after collection in order to obtain a pH between 1 and 2 (usually 2 ml of acid per litre of sample is sufficient). Note the amount of acid added and use the same volume in the preparation of the blank (7.2).

If only dissolved metals are to be determined, filter the sample as soon as possible after collection through a membrane filter of nominal pore diameter 0,45 μm and acidify the filtrate immediately with nitric acid (4.1) in order to obtain a pH between 1 and 2.

Before use, filters shall be thoroughly washed with nitric acid (4.2) and rinsed with water.

7 Procedure

7.1 Test portion

Into a 100 ml one-mark volumetric flask, place a test portion of the acidified sample (6.2) such that it contains 0,2 to 1 mg of metal (see table 1 for the upper limits corresponding to each element). Make up to the mark with water.

7.2 Blank test

Carry out a blank test in parallel with the determination, by the same procedure, using the same quantities of all the reagents as in the sampling and determination, but replacing the test portion by water.

1) Standard solutions are commercially available.

7.3 Preparation of the sets of calibration solutions

Before each batch of determinations, prepare from each of the standard solutions (4.4) at least four calibration solutions covering, for each element, the range of the concentrations to be determined.

Prepare these calibration solutions by diluting standard solutions (4.4) with nitric acid (4.3).

7.4 Calibration and determination

Proceed as follows for each metal being determined. Before carrying out the spectrometric measurements, set up the spectrometer according to the manufacturer's instructions by aspirating a calibration solution (7.3) of the particular metal being determined and using the information in table 4. Optimize the aspiration and flame conditions (aspiration rate, nature of the flame, position of the optical beam in the flame). Adjust the response of the instrument to zero absorbance with water.

Table 4

Element to be determined	Wavelength (nm)	Flame
Cobalt	240,7	Acetylene-air
Nickel	232,0	Oxidizing acetylene-air
Copper	324,7	Oxidizing acetylene-air
Zinc	213,8	Acetylene-air
Cadmium	228,8	Acetylene-air
Lead	283,3 217,0	Acetylene-air

For each metal being determined, aspirate the set of calibration solutions (7.3) and, as zero member, the blank solution (7.2). Plot a graph having the metal contents, in milligrams per litre, of the calibration solutions as abscissae and the corresponding values of absorbance as ordinates. It is advisable that the calibration graph be checked, for example by measuring the absorbance of a calibration solution every 5 samples.

Aspirate the test portion (7.1) into the flame of the burner.

Measure the absorbance of the metal being determined and after each measurement aspirate the nitric acid (4.3) in order to rinse the nebulizer system.

NOTE ON CORRECTION FOR NON-SPECIFIC ABSORPTION

If the spectrometer used is not fitted with a background correction system which supplies automatically a signal corresponding to the specific absorbance A of the metal to be determined, it is necessary to measure the non-specific absorbance A_0 . To do this, proceed as follows.

Choose a spectral line in the proximity of that of the metal to be determined in order to ensure that the difference between the wavelengths of the two spectral lines does not exceed 1 nm.

Use a spectral line of the gas contained in a hollow cathode lamp (argon or neon), or a spectral line emitted by a zirconium or deuterium hollow cathode lamp (see table 5).

Measure the absorbance A_0 corresponding to this spectral line by re-aspirating the test portion.

Calculate the specific absorbance

$$A = A_1 - A_0$$

where A_1 is the total absorbance at the wavelength of analysis.

The flame conditions and the energy assigned to the lamps shall remain unchanged throughout the measurements of the absorbances A_1 and A_0 .

Table 5

Element	A_1 measurement wavelength (nm)	A_0 measurement wavelength (nm)
Cobalt	240,72	241 (D)
Nickel	232,00	232 (D)
Copper	324,75	325 (Zr)
Zinc	213,86	214 (D)
Cadmium	228,80	229 (D)
Lead	283,30	283,7 (Zr)

7.5 Check test

Carry out check tests in order to reveal any matrix effect. To do this, use the method of standard additions.

If a matrix effect is found to be present, the method is not applicable: recommence the determination using either method B or method C or use the results obtained by the method of standard additions.

8 Expression of results

By reference to the calibration graph, determine, for each metal, the concentrations corresponding to the absorbances of the test portion (7.4) and of the blank (7.2).

For each metal being determined, the concentration, expressed in milligrams per litre, of the sample is given by the formula:

$$(e_1 - e_b) \times \frac{100}{V}$$

where

e_1 is the metal concentration, in milligrams per litre, corresponding to the absorbance of the test portion;

e_b is the metal concentration, in milligrams per litre, corresponding to the absorbance of the blank;

V is the volume, in millilitres, of the acidified sample taken for the analysis (see 7.1).

9 Test report

The test report shall contain the following information:

- a reference to this International Standard;
- a reference to the method used;
- complete identification of the sample;
- the results of the determinations;
- any details not specified in this International Standard or which are optional, as well as any factor which may have affected the results.

Section two : Method B — Determination by flame atomic absorption spectrometry after chelation (APDC) and extraction (MIBK)

10 Principle

Formation of a complex between the metals being determined and ammonium 1-pyrrolidinedithiocarbamate (APDC) and extraction at pH 2,5 with methyl-isobutylketone (MIBK).

Determination of the metals in this organic phase by flame atomic absorption spectrometry.

11 Reagents

See clause 4.

11.1 Nitric acid, $\rho = 1,4$ g/ml.

11.2 Sodium hydroxide, $c(\text{NaOH}) = 2,5$ mol/l.

With care, dissolve 100 g of sodium hydroxide in water and dilute to 1 litre.

11.3 Hydrochloric acid, $c(\text{HCl}) = 0,3$ mol/l.

With care, mix 25 ml of concentrated hydrochloric acid ($\rho = 1,19$ g/ml) with water and dilute to 1 litre.

11.4 Methyl-isobutylketone (MIBK).¹⁾

11.5 Ammonium 1-pyrrolidinedithiocarbamate (APDC)²⁾, 20 g/l solution.

Dissolve 2,0 g of APDC in water. Make up the volume to 100 ml with water and mix. Filter the solution if a precipitate is present. If the solution is coloured, purify it by repeated extraction with MIBK (11.4) until the solution is colourless.

Prepare this solution freshly for each batch of samples.

11.6 Bromophenol blue, indicator solution, 1 g of bromophenol blue per litre of 50 % (V/V) ethanol solution.

11.7 Metals, standard solutions, corresponding to 1,000 g of metal per litre. See 4.4.

12 Apparatus

See clause 5.

13 Sampling and samples

See clause 6.

14 Procedure

14.1 Test portion

Place in a 100 ml one-mark volumetric flask a test portion of the acidified sample (see clause 6) containing 5 to 20 μg of the metal being determined (see table 2 for the upper limits corresponding to each element). Make up to the mark with water.

14.2 Chelation and extraction

Place the test portion (14.1) and 100 ml of each of the calibration solutions (14.4) into a series of 250 ml separating funnels fitted with polytetrafluoroethylene (PTFE) taps.

Add to each funnel 2 to 3 drops of bromophenol blue indicator (11.6) and sodium hydroxide (11.2) until a blue colour persists.

While stirring, add dropwise hydrochloric acid (11.3) until the blue colour just disappears. Then add 2 ml of hydrochloric acid (11.3) in excess. The pH value shall then be 2,3 to 2,5. (See note 1.)

Add 5 ml of APDC (11.5), mix then add 10,0 ml of MIBK (11.4). Shake vigorously for 2 min. The pH shall be approximately 2,8.

Allow the mixture to settle for at least 1 h away from light or heat in the stoppered funnel. The settling time shall be strictly the same for all the solutions. Collect the organic layer taking care to avoid any trace of the aqueous phase (centrifuge if necessary). (See note 2.)

NOTES

1 A pH meter may be used in place of the indicator.

2 The settling period may be prolonged without disadvantage if it takes place in the dark at a temperature of about 5 °C. In this case it may not be necessary to centrifuge the organic phase.

14.3 Blank test

Carry out a blank test in parallel with the determination, by the same procedure (14.2), using the same quantities of all the reagents as in the sampling and chelation and extraction, but replacing the test portion by water.

1) 4-Methyl-2-pentanone.

2) Ammonium-pyrrolidinocarbodithioate.

Preparation of the sets of calibration solutions

with water¹⁾ immediately before use, each of the solutions (4.4) corresponding to the elements to be determined, in order to obtain diluted solutions containing 10 mg of metal per litre,

100 ml one-mark volumetric flask, place

5 ml of each of the zinc and cadmium solutions that contain 10 mg/l of the respective metal;

20 ml of each of the copper, cobalt, nickel and lead solutions that contain 10 mg/l of the respective metal;

0,5 ml of nitric acid (11.1).

Fill up to the mark with water. This is solution S. Prepare all your calibration solutions by diluting solution S with water to cover the following ranges of concentrations:

1, Cd = 0 to 50 µg/l

2, Co, Ni, Pb = 0 to 200 µg/l

Dilute each calibration solution by adding the same nitric acid (11.1) which has been added to preserve the samples (see 6.2). The volume added shall be such that the concentrations of nitric acid are the same in the sample and in the calibration solutions.

Calibration and determination

Proceed as follows for each metal being determined. Before carrying out the spectrometric measurements, set up the spectrometer according to the manufacturer's instructions by adding the organic extract (14.2) of a calibration solution of the metal being determined and using information in table 4. Normalize the aspiration and flame conditions as before (7.4). Adjust the response of the instrument to zero absorbance with the blank solution (11.4).

For each metal being determined, aspirate the set of organic extracts of the calibration solutions. Plot a graph having the metal contents, in micrograms per litre, of the calibration solutions as abscissae and the corresponding values of absorbance as ordinates. It is advisable that the calibration graph be checked, for example by measuring the absorbance of a calibration solution every 5 samples.

Aspirate the organic extract of the test portion.

Measure the absorbance of the metal being determined and after each measurement aspirate MIBK in order to rinse the nebulizer system.

For correction of non-specific absorption see the note to 7.4.

NOTE — It is very important to protect the organic solutions from heat and light because the complexes of cobalt, copper, zinc and especially cadmium are unstable in MIBK. Cadmium must be measured immediately. The other metals can be stored for a few hours.

15 Expression of results

15.1 Calculation

By reference to the calibration graph, determine, for each metal, the concentrations corresponding to the absorbances of the test portion and of the blank.

For each metal being determined, the concentration, expressed in micrograms per litre, of the sample is given by the formula:

$$(q_t - q_b) \times \frac{100}{V}$$

where

q_t is the metal concentration, in micrograms per litre, corresponding to the absorbance of the test portion;

q_b is the metal concentration, in micrograms per litre, corresponding to the absorbance of the blank;

V is the volume, in millilitres, of the acidified sample taken for the analysis (see 14.1).

15.2 Precision

An international interlaboratory trial was organized in 1981 in order to compare the repeatability and reproducibility of the two methods with extraction (methods B and C).

The composition of the two samples analysed was as given in table 6.

Table 6

	Sample L (low level) (µg/l)	Sample H (high level) (µg/l)
Lead	20	100
Cadmium	4	30
Copper	6	40
Cobalt	5	120
Nickel	10	100

The statistical analysis of results according to ISO 5725 is given in table 7.

15.3 Interferences

Other substances when present at concentrations of less than 5 mg/l do not normally interfere.

16 Test report

See clause 9.

When determining metals in sea water or other waters containing a high concentration of sodium chloride, prepare the calibration solution and blank solution with a water of the same content of NaCl as the water being analysed.

Table 7

Metal	Lead		Cadmium		Copper		Cobalt		Nickel	
	L	H	L	H	L	H	L	H	L	H
Number of participating laboratories	14	14	14	14	14	14	14	14	14	14
Number of retained laboratories after statistical elimination	14	12	11	13	12	14	13	14	14	14
Mean ($\mu\text{g/l}$)	19,7	96	4	30,2	5,7	40,8	5,1	121,3	10,7	103,2
Repeatability										
Standard deviation, σ_r	1,5	2,6	0,1	0,7	0,2	1,7	0,4	1,9	0,4	2,3
Coefficient of variation of repeatability	7,6 %	2,7 %	2,5 %	2,3 %	3,5 %	4,2 %	7,8 %	1,6 %	3,7 %	2,2 %
Repeatability, $r (= 2,83 \sigma_r)$	4,24	7,36	0,28	1,98	0,57	4,8	1,13	5,38	1,13	6,51
Reproducibility										
Standard deviation, σ_R	3,2	5,3	0,3	1,3	0,7	5,9	1,4	7,6	1,4	16,2
Coefficient of variation of reproducibility	16,2 %	5,5 %	7,5 %	4,3 %	12,3 %	14,5 %	27,5 %	6,3 %	13,1 %	15,7 %
Reproducibility, $R (= 2,83 \sigma_R)$	9,05	15	0,85	3,68	1,98	16,7	3,96	21,51	3,96	45,85

Section three : Method C — Determination by flame atomic absorption spectrometry after chelation (HMA-HMDC) and extraction (DIPK-xylene)

17 Principle

Formation of a complex between metals and hexamethylene-ammonium-hexamethylenedithiocarbamate (HMA-HMDC) and extraction with diisopropylketone-xylene in a buffered medium of pH value 2 to 4.

Determination of the metals in this organic phase by flame atomic absorption spectrometry.

18 Reagents

See clause 4.

18.1 Nitric acid, $\rho = 1,4$ g/ml.

18.2 Hexamethyleneammonium-hexamethylenedithiocarbamate (HMA-HMDC).¹⁾

To a solution of 224 ml of distilled hexamethylene imine (bp 136 to 139 °C) in 300 ml of xylene, which is cooled by an ice-bath, add within 30 min and with constant stirring and cooling, 60 ml of distilled carbon disulfide (bp 46,2 °C).

Continue cooling and stirring for 1 h. Filter the solution and collect the flocculent white precipitate; wash it three times with diethylether and dry between two filter papers.

18.3 HMA-HMDC, 6,8 g/l extraction solution.

Dissolve, in a dry 250 ml one-mark volumetric flask, 1,7 g of HMA-HMDC (18.2) in 75 ml of xylene, heating gently. Make up to the mark with diisopropylketone²⁾ (DIPK) (bp 124,5 °C).

This solution is stable for a week if stored at 5 °C away from light.

18.4 HMA-HMDC, 55 g/l solution in methanol.

In a dry 100 ml one-mark volumetric flask, dissolve 5,5 g of HMA-HMDC (18.2) in methanol, heating gently. Cool to room temperature and make up to the mark with methanol.

18.5 Formate, buffer solution.

Dissolve 368 g of formic acid [98 to 100 % (m/m)] and 14 g of citric acid monohydrate in 350 ml of water. Slowly add, with constant stirring and cooling, 243 g of sodium hydroxide. Add

50 mg of *m*-cresolsulfonephthalein (metacresol purple). Purify this solution by two consecutive extractions with extraction solution (18.3), with constant stirring.

18.6 Metals, standard solutions, corresponding to 1,000 g of metal per litre.

Dissolve jointly 1,000 g of each metal to be determined in nitric acid (18.1) by heating until complete dissolution. Cool and make up to 1 000 ml with water. The acid concentration of this solution shall be approximately 0,1 to 0,5 mol/l.

When preparing the standard solutions, it is also permissible to use metal salts of accurately known composition.

18.7 Metals, organic standard solution, corresponding to 50 mg of metal per litre.

In a dry 100 ml one-mark volumetric flask, place 5 ml of aqueous standard solution (18.6). Add 50 ml of formic acid [98 to 100 % (m/m)] and 0,2 to 0,5 g of citric acid monohydrate. Make up to the mark with diisopropylketone.

19 Apparatus

The apparatus specified in clause 5, and

Microlitre pipettes.

Clean the plastic tips of microlitre pipettes by soaking in nitric acid (4.2) for several hours. Avoid temperatures above 40 °C. Rinse with water before use.

20 Sampling and samples

See clause 6.

21 Procedure

21.1 Test portion

The test portion of the acidified sample (see clause 6) is generally 400 ml.

Other volumes which give a ratio of aqueous phase to organic phase of up to 50 to 1 by volume may be used when it is desired to obtain greater or smaller enrichment factors.

1) This reagent is commercially available.

2) 2,4-Dimethyl-3-pentanone.

21.2 Chelation and extraction

Place the test portion (21.1) in a 500 ml one-mark volumetric flask. Add 20 ml of formate buffer solution (18.5). The colour of the indicator shall be a pure yellow. If a red colour appears, add an additional 20 ml of formate buffer solution.

Add 2,0 ml of HMA-HMDC solution in methanol (18.4), shake and allow to stand for 3 to 5 min.

Add 20,0 ml of extraction solution (18.3) and shake the flask vigorously for at least 3 min.

Allow the mixture to settle for 10 to 15 min in order to obtain a good separation of the layers. Then carefully add water until the organic layer is completely in the neck of the flask.

Aspiration of the organic layer for the determination (21.5) may be done directly from the neck of the flask.

If the organic layer has to be kept for a longer time, pipette it off, taking care to avoid any trace of the aqueous phase, and store in a cool dark place.

21.3 Blank test

Carry out a blank test in parallel with the determination, by the same procedure (21.2), using the same quantities of all the reagents as in the sampling and chelation and extraction, but replacing the test portion by nitric acid (4.3).

21.4 Preparation of the sets of calibration solutions

21.4.1 Aqueous solutions

Before each batch of determinations, prepare at least four aqueous calibration solutions covering the range of the concentrations to be determined. Prepare these calibration solutions by diluting the aqueous standard solution (18.6) with nitric acid (4.3).

NOTE — These sets of aqueous solutions are used for verification of completeness of extraction. Laboratories which are not familiar with extraction are advised to check complete extraction following the procedure described in annex B.

21.4.2 Organic solutions

Immediately prior to use, prepare at least four organic calibration solutions covering the range of the concentrations to be determined.

Prepare these calibration solutions by diluting the organic standard solution (18.7) with extraction solution (18.3) using dry 25 ml one-mark volumetric flasks and microlitre pipettes (clause 19).

21.5 Calibration and determination

Proceed as follows for each metal. Before carrying out the spectrometric measurements, set up the spectrometer according to the manufacturer's instructions by aspirating one of the

organic calibration solutions (21.4.2) and using the information in table 4. Optimize the aspiration and flame conditions as before (7.4). Adjust the response of the instrument to zero absorbance with extraction solution (18.3).

For each metal being determined, aspirate the set of organic calibration solutions (21.4.2). Plot a graph having the metal contents, in micrograms per litre, of the organic calibration solutions as abscissae and the corresponding values of absorbance as ordinates.

Aspirate the organic extract of the test portion (21.2).

Measure the absorbance of the metal to be determined. After each measurement rinse the nebulizer system by aspirating with methanol to avoid clogging.

If necessary, correct for non-specific absorption (see the note to 7.4).

22 Expression of results

22.1 Calculation

By reference to the calibration graph, determine, for each metal, the concentrations corresponding to the absorbances of the test portion and of the blank.

For each metal being determined, the concentration, expressed in micrograms per litre, of the sample is given by the formula:

$$(\rho_1 - \rho_b) \times \frac{20}{V}$$

where

ρ_1 is the metal concentration, in micrograms per litre, corresponding to the absorbance of the test portion;

ρ_b is the metal concentration, in micrograms per litre, corresponding to the absorbance of the blank;

V is the volume, in millilitres, of the acidified sample taken for the analysis (see 21.1).

22.2 Repeatability and reproducibility

An international interlaboratory trial was organized in 1981 in order to compare the repeatability and reproducibility of the two methods with extractions (methods B and C).

The compositions of the two samples analysed were as given in table 6.

The statistical analysis of results according to ISO 5725 is given in table 8.

22.3 Interferences

A total concentration of heavy metals, iron included, up to 20 mg/l is tolerable. If the total concentration of heavy metals exceeds 20 mg/l, a ratio of test portion to extraction solution smaller than 20 to 1 by volume shall be taken.

Table 8

Metal	Lead		Cadmium		Copper		Cobalt		Nickel	
	L	H	L	H	L	H	L	H	L	H
Level										
Number of participating laboratories	16	16	16	16	16	16	15	10	15	10
Number of retained laboratories after statistical elimination	14	14	13	13	15	16	14	14	11	14
Mean ($\mu\text{g/l}$)	20,3	97,7	4	29,8	6,4	41	5,8	115,8	10,9	100,2
Repeatability										
Standard deviation, σ_r	1,06	3,8	0,3	0,8	0,5	3,3	0,6	3,6	1,8	4,7
Coefficient of variation of repeatability	5,2 %	3,9 %	7,5 %	2,7 %	7,8 %	8,0 %	10,3 %	3,1 %	16,5 %	4,7 %
Repeatability, $r (= 2,83 \sigma_r)$	3,0	10,7	0,85	2,26	1,41	9,34	1,7	10,2	5,1	13,3
Reproducibility										
Standard deviation, σ_R	2,8	3,4	0,4	2,7	1,1	4,8	1,2	8,2	4	13,7
Coefficient of variation of reproducibility	13,8 %	3,5 %	10 %	9,1 %	17,2 %	11,7 %	20,7 %	7,1 %	36,7 %	13,7 %
Reproducibility, $R (= 2,83 \sigma_R)$	7,9	9,62	1,13	7,64	3,11	13,6	3,4	23,21	11,3	38,8

The tolerable concentration of nitriloacetic acid is 250 mg/l. Ethylenediaminetetraacetic acid (EDTA) interferes in the extraction of nickel; concentration of 25 mg/l of ethylenediaminetetraacetic acid disodium salt dihydrate ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8\text{Na}_2 \cdot 2\text{H}_2\text{O}$) is tolerable in the extraction of the five other metals.

Humic acid contained in neutral water samples precipitates upon acidification. This precipitate should be removed by filtration; it does not retain heavy metals. Extraction of the

heavy metals from the filtrate as hexamethylene dithiocarbamates with diisopropylketone-xylene can be performed with complete recovery.

23 Test report

See clause 9.

Annex A

Pretreatment of the sample when determining total metals

(This annex forms an integral part of the standard.)

A.0 For the majority of samples, mineralization using hydrochloric or nitric acids will be satisfactory. However, occasionally, for example with heavily polluted waste waters, a more vigorous procedure may be required.

The alternative procedures of mineralization which follow are given as examples.

A.1 Add 5 ml of hydrochloric acid ($\rho = 1,19$ g/ml) for each 100 ml of test portion.

Heat in a steam-bath until the volume has been reduced to between 15 and 20 ml, making certain that the sample does not boil.

Cool and filter to remove insoluble materials that could clog the nebulizer. Collect the filtrate in a 100 ml volumetric flask.

Wash the filter several times with water.

A.2 Add 4 ml of 15 mol/l nitric acid to 100 ml of the sample and heat until the volume is reduced to 50 ml.

Place the treated sample in a boiling flask. Add 12 ml of hydrochloric acid ($\rho = 1,19$ g/ml). Connect the boiling flask to a condenser and reflux the solution for 2,5 h.

Cool and filter to remove insoluble materials that could clog the nebulizer. Collect the filtrate in a 100 ml one-mark volumetric flask.

Wash the condenser and filter several times with water, add this to the contents of the volumetric flask and make up to the mark with water.

Annex B

Checking complete extraction (Method C)

(This annex forms an integral part of the standard.)

Before analysing samples, prepare in parallel with the test at least two aqueous calibration solutions (21.4.1) with respective concentrations which cover the expected range of the sample.

Chelate and extract these aqueous calibration solutions as directed in 21.2.

Aspirate the organic extracts into the flame and measure the absorbances of the organic extract as directed in 21.5.

Prepare in parallel at least two organic calibration solutions (21.4.2), the concentrations of which are respectively 20 and 50 times higher (depending on the enrichment factor chosen) than the concentrations of the corresponding aqueous calibration solutions. Aspirate these organic solutions and measure the absorbances as directed in 21.5.

Extraction is complete if the organic extracts of the aqueous calibration solutions give the same absorbance values as the organic calibration solutions.



British Standard Methods of testing

Water used in industry

Part 120. Suspended solids : gravimetric method (after filtration)

Méthodes d'essai de l'eau à usage industriel

Partie 120. Matières en suspension : méthode gravimétrique (après filtration)

Prüfverfahren für Wasser für industrielle Zwecke

Teil 120. Schwebestoffe : gravimetrisches Verfahren (nach Filtrierung)

IMPORTANT NOTE. It is essential that this Part be read in conjunction with the information in Part 100 of this standard, 'Foreword, scope and general requirements', which is published separately.

0. Introduction

BS 2690 : Parts 118 to 122 will together supersede BS 2690 : Part 9 : 1970. This Part supersedes clause 4 which is being deleted by amendment and Part 9 will be withdrawn when the publication of all of these five Parts is complete.

1. Scope

The method described is for the determination of suspended solids in industrial water.

2. Range

Approximately 0.5 mg to 100 mg of suspended solids.

3. Principle

The term 'suspended solids' is intended to mean solid material that is separated from the sample when the operations described in clause 5 are carried out. It is recognized that some solids not in true solution may, by reason of their finely dispersed or colloidal condition, escape inclusion in the value reported.

The two procedures described in 5.1 and 5.2 both use glass fibre filter papers, suitable for solids as small as approximately 2 μm to 3 μm in diameter. If smaller particles are to be evaluated, as in the assay of demineralized water for high pressure boiler feed, then membrane filters of 0.45 μm pore size or less should be used.

4. Apparatus

4.1 Filter funnel, either

- (a) a 70 mm Hahn or Hartley pattern Buchner funnel (recommended for the determination of low levels of

suspended solids, i.e. less than 20 mg solids in the test portion), or

- (b) a porcelain Gooch crucible with a capacity of about 25 ml, having perforations at least 0.8 mm in diameter.

4.2 *Ultra-fine glass fibre filter papers*^{*}, to fit the Hahn or Hartley pattern Buchner funnel or the Gooch crucible.

4.3 *Vacuum filtration apparatus.*

5. Procedure

5.1 **Using a Hahn or Hartley pattern Buchner funnel.** Clip a glass fibre filter paper into the funnel and, using slight suction, wash it with about 100 ml of water. When free from excess water, remove the paper carefully, place it on a watch glass and dry in an oven at 105 °C to 110 °C for 1 h. Allow the paper and watch glass to cool in a desiccator and weigh the paper only.

Clip the paper into the funnel and saturate it with water. Measure a suitable volume of the well mixed sample of water containing not more than about 20 mg of suspended solids and filter it, under slight suction, through the tared paper, ensuring that the solids are transferred to the filter.

Suspended solids in a finely divided form may block the pores of the filter and so retard filtration. In this case, centrifuge the measured sample until the supernatant liquor is clear. Then decant the clear liquor and filter the residual slurry.

Wash the residue on the filter three times with 5 ml portions of water, allowing it to drain free from water after each wash (see note 1 to 5.2). Carefully remove the paper, place it on a watch glass and dry in an oven at 105 °C to 110 °C for at least 1 h. Allow the paper and watch glass to cool in a desiccator, and weigh the paper and residue.

^{*}Whatman GF/C papers are suitable.

5.2 Using a porcelain Gooch crucible. Fit a glass fibre filter paper into the Gooch crucible and, using slight suction, wash it with about 100 ml of water. When free from excess water, dry the Gooch crucible and paper in an oven at 105 °C to 110 °C for 1 h, allow to cool in a desiccator and weigh.

Measure a suitable volume of the well mixed sample of water containing not more than about 100 mg of suspended solids and filter it, under slight suction, through the tared paper and crucible, ensuring that the solids are transferred to the filter.

Suspended solids in a finely divided form may block the pores of the filter and so retard filtration. In this case, centrifuge the measured sample until the supernatant liquor is clear. Then decant the clear liquor and filter the residual slurry.

Wash the residue on the filter three times with 5 ml portions of water, allowing it to drain free from water after each wash (see note 1). Dry the Gooch crucible and contents in an oven at 105 °C to 110 °C for at least 1 h, allow to cool in a desiccator and weigh (see note 2).

NOTE 1. The aim of the washing procedure is to remove the small amounts of residual dissolved solids. The amount of water is kept to a minimum to avoid dissolving sparingly soluble solids. If oil is present in the sample, it may be retained on the filter. In such cases, remove the bulk of this oil by washing the residue on the

filter first with ethanol and then with a suitable organic solvent, e.g. light petroleum, before drying at 105 °C to 110 °C.

Further information on errors is given in Water Research Centre Technical Report No. 127 'Determination of suspended solids and ash in water by filtration and ignition'.

NOTE 2. An indication of organic matter present in the suspended solids can be obtained from the difference between the determination in accordance with 5.2 and one in which the residue is heated to 475 °C to 500 °C. Care should be taken not to exceed 500 °C, particularly during the heating of the glass fibre filter papers before the filtration stage, because temperatures in excess of this value may cause their deterioration. In interpreting the results obtained, it should be remembered that decomposition of some inorganic compounds can take place at 475 °C to 500 °C.

For this determination use the Gooch crucible procedure, washing the filter paper with 100 ml of water, followed by drying at 475 °C to 500 °C for 1 h, cooling in a desiccator and weighing.

After filtering the solids, first dry the Gooch crucible with contents at 105 °C to 110 °C for 1 h, allow to cool in a desiccator and weigh. Then heat the Gooch crucible with contents to 475 °C to 500 °C for 1 h, allow to cool in desiccator and weigh.

6. Calculation

$$\text{Suspended solids, dried at } 105\text{ }^{\circ}\text{C (mg/l)} = \frac{m}{v} \times 1000$$

where

m is the mass of residue (mg), and

v is the volume of sample (ml).

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APPENDIX II;
B.S 6068: SECTION 6.3:1986

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Table — Techniques generally suitable for the preservation of samples

(The information in this table is only a general guide to the preservation of samples. The complex nature of natural and waste waters necessitates, before analysis, a verification of the stability of each type of sample treated according to the methods proposed below.)

A. Physico-chemical and chemical analyses					
1	2	3	4	5	6
Parameter to be studied	Type of container P = Polyethylene G = Glass BG = Borosilicate glass	Preservation technique	Place of analysis	Maximum recommended preservation time before analysis (If a preservation period is not specified, it is generally unimportant. The indication "1 month" represents preservation without particular difficulty.)	Comments
Acidity and alkalinity	P or G	Cooling to between 2 and 5 °C	Laboratory	24 h	Samples should preferably be analysed at the spot where the sample is taken (particularly for samples high in dissolved gases).
Aluminium filterable ¹¹	P	Filtration at the place of sampling and acidification of the filtrate to pH < 2	Laboratory	1 month	The filterable ¹¹ aluminium and that adhering to suspended matter may be determined from the same sample.
adhering to suspended matter		Filtration at the place of sampling	Laboratory	1 month	The filterable aluminium on the acidified filtrate and the aluminium adhering to suspended matter may be determined from the filter residue.
total		Acidification to pH < 2	Laboratory	1 month	
Arsenic	P or G	Acidification to pH < 2	Laboratory		
	P	Alkalinization to pH = 12	Laboratory		This technique should be used if arsenides are assumed to be present in samples of domestic or industrial waste water.
Barium	P or BG	See Aluminium			Do not use H ₂ SO ₄ .
BOD	P or G (Glass is preferable in the case of low BOD.)	Cooling to between 2 and 5 °C and storage in the dark	Laboratory	As soon as possible	
		Freezing to - 20 °C	Laboratory	1 month	
Boron and borates	P		Laboratory	Several months	
Bromides and bromine compounds	P or G	Cooling to between 2 and 5 °C	Laboratory	As soon as possible	Samples should be kept out of direct sunlight.
Cadmium	P or BG	See Aluminium			
Calcium	P or G	—	Laboratory	24 h	
		Acidification to pH < 2	Laboratory	Several months	Acidification (do not use H ₂ SO ₄) permits determination of the calcium from the same sample as the other metals.
Carbon dioxide	P or G	—	On site		

Table — Techniques generally suitable for the preservation of samples (continued)

1	2	3	4	5	6
Carbon, organic	G	Acidification to pH < 2 with H ₂ SO ₄ and cooling to between 2 and 5 °C	Laboratory	24 h	The preservation technique will depend on the method of analysis to be used. The test should be carried out as soon as possible. Freezing (- 20 °C) may be used in certain cases.
Chlorides	P or G	—	Laboratory	Several months	
Chlorine, residual	P or G	—	On site	—	The analysis shall be carried out on site.
Chlorophyll	P or G	Cooling to 4 °C	Laboratory	24 h	
		After filtration and freezing of the residue	Laboratory	1 month	
Chromium(VI)	P or BG	Cooling to between 2 and 5 °C	Laboratory	As soon as possible	
Chromium, total	P or BG	See Aluminium			
Cobalt	P or BG	See Aluminium			
COD	P or G (Glass is preferable in the case of low COD.)	Cooling to between 2 and 5 °C and storage in the dark	Laboratory	As soon as possible	Acidification is particularly recommended when the COD is due to the presence of organic materials.
		Acidification to pH < 2 with H ₂ SO ₄	Laboratory	2 days	
		Freezing to - 20 °C	Laboratory	1 month	
Colour	P or G	—	On site	—	
		Cooling to between 2 and 5 °C and storage in the dark	Laboratory	24 h	
Conductivity	P or G	Cooling to between 2 and 5 °C	Laboratory	24 h	The test should preferably be carried out on site.
Copper	P or BG	See Aluminium			
Cyanides, easily liberatable	P	The preservation technique will depend on the method of analysis to be used.			
Cyanides, total	P	Alkalinization to pH > 12 with NaOH	Laboratory	24 h	
Detergents	See Surface active agents				
Diffusion index	See Turbidity				
Dry extract	See Total residue				
Fluorescein	See Fluorescent tracers				
Fluorescent tracers	P (preferably an opaque container)	—	Laboratory	1 month	
Fluorides	P	—	Laboratory	Several months, provided that the sample is neutral	
Greases, oils, hydrocarbons	Glass washed in solvents	Acidification to pH < 2, extraction on site where practicable	Laboratory	24 h	It is recommended that, immediately after sampling, the extraction agent used in the method of analysis be added, or that extraction be carried out on site.
Heavy metals (except mercury)	P or BG	See Aluminium			

Table — Techniques generally suitable for the preservation of samples (continued)

1	2	3	4	5	6
Hydrazine	G	Acidification with HCl to 1 mol/l (100 ml per litre of sample) and storage in the dark	Laboratory	24 h	
Hydrogen ¹ carbonates	See Alkalinity				
Iodides	Inactivic glass	Cooling to between 2 and 5 °C _i	Laboratory	24 h	Samples should be kept out of direct sunlight.
		Alkalinization to pH 8	Laboratory	1 month	
Iron(II)	P or BG	Acidification to pH < 2 with HCl and exclusion of atmospheric oxygen	On site	1 week	
Iron, total	P or BG	See Aluminium			
Lead	P or BG	See Aluminium			Do not use H ₂ SO ₄ .
Lithium	P	—	Laboratory	7 days	
		Acidification to pH < 2	Laboratory	Several months	Acidification permits determination of the lithium from the same sample as the other metals.
Magnesium	P or BG	See Calcium			
Manganese	P or BG	See Aluminium			
Mercury, total	BG	Acidification to pH < 2 with HNO ₃ and addition of K ₂ Cr ₂ O ₇ [0,05 % (m/m) final concentration]	Laboratory	Several months	Particular care is needed to ensure that the sample containers are free from contamination.
Nickel	P or BG	See Aluminium			
Nitrogen, ammoniacal and Kjeldahl	P or G	Acidification to pH < 2 with H ₂ SO ₄ and cooling to between 2 and 5 °C	Laboratory	24 h	The addition of a bactericide (for example allylthiourea, though the addition of an excess should be avoided) may possibly be considered in order to block the metabolism of the nitrifying bacteria. In this case use a glass container.
		Cooling to between 2 and 5 °C	Laboratory	6 h	For concentrations less than 1 mg/l, it is necessary to carry out analysis on site.
Nitrogen as nitrate	P or G	Acidification to pH < 2 and cooling to between 2 and 5 °C	Laboratory	24 h	For certain waste waters, the sample cannot be preserved and it is necessary to carry out analysis on site.
Nitrogen as nitrite	P or G	Cooling to between 2 and 5 °C	Laboratory	As soon as possible	For certain waste waters, the sample cannot be preserved and it is necessary to carry out analysis on site.
Odour	G	—	Laboratory	6 h	The test should preferably be carried out on site.

Table — Techniques generally suitable for the preservation of samples (continued)

1	2	3	4	5	6
Orthophosphates	B or G	Cooling to between 2 and 5 °C	Laboratory	24 h	The analysis should be carried out as soon as possible. The sample should be filtered immediately for the analysis of dissolved phosphate.
Oxygen	P or G	—	On site	—	Fix the oxygen in accordance with the method of analysis used.
		Fixing of the oxygen on site and storage in the dark	Laboratory	4 days at most	
Ozone	—	—	On site	—	
Pesticides, organochloride	G	Cooling to 4 °C	Laboratory	7 days	It is recommended that, immediately after sampling, the extraction agent used in the method of analysis be added, or that extraction be carried out on site.
Pesticides, organophosphorus	G	Cooling to 4 °C	Laboratory	24 h	It is recommended that, immediately after sampling, the extraction agent used in the method of analysis be added, or that extraction be carried out on site.
Petroleum and derivatives	See Greases, oils and hydrocarbons				
pH	P or G	—	On site		The test should be carried out as soon as possible and preferably immediately on site after sampling.
		Transportation at a lower temperature than the initial temperature	Laboratory	6 h	
Phenols	BG	Inhibition of biochemical oxidation by CuSO_4 and acidification with H_3PO_4 or alkalization with NaOH to $\text{pH} > 11$	Laboratory	24 h	The preservation technique will depend on the method of analysis to be used.
Phosphorus, total	B or G	—	Laboratory	24 h	
		Acidification to $\text{pH} < 2$ with H_2SO_4	Laboratory	Several months	
Potassium	See Lithium				
Putrescibility (methylene blue test)	G	Transportation at a lower temperature than the initial temperature	Laboratory	24 h	The test should be carried out as soon as possible and preferably on site at 20 °C.
Selenium	G or BG	Alkalization to $\text{pH} > 11$ with NaOH	Laboratory	Several months	
Silicates	P	Filtration and acidification to $\text{pH} < 2$ with H_2SO_4 and cooling to between 2 and 5 °C	Laboratory	24 h	
Silicon, total	P	—	Laboratory	Several months	
Silver	P or BG	See Aluminium			Do not use HCl.
Sodium	See Lithium				

Table — Techniques generally suitable for the preservation of samples (continued)

1	2	3	4	5	6
Sugars	P or G	Cooling to between 2 and 5 °C	Laboratory	24 h	This preservation technique is related to the glucose oxidase enzymic determination method.
		Addition of 30 % (m/m) formaldehyde (5 ml per 100 ml of sample) and cooling to between 2 and 5 °C	Laboratory	1 month	
* Sulfates	P or G	Cooling to between 2 and 5 °C	Laboratory	1 week	
Sulfides	P or G	Treatment with 2 ml of 1 mol/l (CH ₃ CO ₂) ₂ Zn and alkalization with 2 ml of 1 mol/l NaOH	Laboratory	1 week	
Sulfites	P or G	Fixing on site by addition of 1 ml of a 2,5 % (m/m) solution of EDTA per 100 ml of sample	Laboratory	1 week	
Surface active agents, ionic	G	Acidification to pH < 2 with H ₂ SO ₄ and cooling to between 2 and 5 °C	Laboratory	48 h	
Surface active agents, non-ionic	G	Addition of 40 % (V/V) formaldehyde to give a 1 % (V/V) solution; cool to between 2 and 5 °C and ensure sampling container is completely filled.	Laboratory	1 month	
* Suspended and sedimentary matter	P or G	—	Laboratory	24 h	The test should be carried out as soon as possible and preferably on site.
Tin	P or BG	See Aluminium			
* Total hardness	See Calcium		1 to 3 days		
Total residue (dry extract)	P or G	Cooling to between 2 and 5 °C	Laboratory	24 h	The sample should be placed in the capsule used for the test as soon as possible.
Turbidity	P or G	—	Laboratory	As soon as possible	The test should preferably be carried out on site.
Uranium	P or BG	See Aluminium			
* Zinc	P or BG	See Aluminium			

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