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Workplace air — Determination of hexavalent chromium in airborne particulate matter — Method by ion chromatography and spectrophotometric measurement using diphenyl carbazide

Air des lieux de travail — Détermination du chrome hexavalent dans les particules en suspension dans l'air — Méthode par chromatographie ionique et détection spectrophotométrique avec diphényl carbazide

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 16740 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

Introduction

The health of workers in many industries is at risk through exposure by inhalation of hexavalent chromium compounds. Industrial hygienists and other public health professionals need to determine the effectiveness of measures taken to control workers' exposure, and this is generally achieved by making workplace air measurements. This International Standard has been published in order to make available a method for making valid exposure measurements for hexavalent chromium compounds used in industry. It will be of benefit to agencies concerned with health and safety at work; industrial hygienists and other public health professionals; analytical laboratories; industrial users of hexavalent chromium compounds and their workers.

It has been assumed in the drafting of this International Standard that the execution of its provisions, and the interpretation of the results obtained, is entrusted to appropriately qualified and experienced people.

INTERNATIONAL STANDARD **ISO 16740:2005(E)**

Workplace air — Determination of hexavalent chromium in airborne particulate matter — Method by ion chromatography and spectrophotometric measurement using diphenyl carbazide

1 Scope

This International Standard specifies a method for the determination of the time-weighted average mass concentration of hexavalent chromium in workplace air.

Separate sample preparation methods are specified for the extraction of soluble and insoluble hexavalent chromium. The method for insoluble hexavalent chromium can also be used to prepare samples for determination of total hexavalent chromium, if desired.

This International Standard is applicable to the personal sampling of the inhalable fraction of airborne particles, as defined in ISO 7708, and to static (area) sampling. The analytical method is applicable to the determination of masses of 0,01 µg to 10 µg of hexavalent chromium per sample, without dilution.

The concentration range of hexavalent chromium in air for which the measuring procedure is applicable is determined by the sampling method selected by the user (see 10.1). For a 1 m^3 air sample, without sample dilution, the working range is approximately 0,01 $\mu g \cdot m^{-3}$ to 10 $\mu g \cdot m^{-3}$.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 648, *Laboratory glassware — One-mark pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 3585, *Borosilicate glass 3.3 — Properties*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 7708:1995, *Air quality — Particle size fraction definitions for health-related sampling*

ISO 8655-1, *Piston-operated volumetric apparatus — Part 1: Terminology, general requirements and user recommendations*

ISO 8655-2, *Piston-operated volumetric apparatus — Part 2: Piston pipettes*

ISO 8655-5, *Piston-operated volumetric apparatus — Part 5: Dispensers*

ISO 8655-6, *Piston-operated volumetric apparatus — Part 6: Gravimetric methods for the determination of measurement error*

EN 13205, *Workplace atmospheres — Assessment of performance of instruments for measurement of airborne particle concentrations*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1 General definitions

3.1.1
chemical agent
any chemical element or compound, on its own or admixed, as it occurs in the natural state or as produced, used or released, including release as waste by any work activity, whether or not produced intentionally and whether or not placed on the market

[EN 1540 [1]]

3.1.2
breathing zone
⟨general definition⟩ space around the worker's face from where he or she takes his or her breath

3.1.3
breathing zone
⟨technical definition⟩ hemisphere (generally accepted to be 0,3 m in radius) extending in front of the human face, centred on the midpoint of a line joining the ears; the base of the hemisphere is a plane through this line, the top of the head and the larynx

NOTE 1 This definition is not applicable when respiratory protective equipment is used.

NOTE 2 Adapted from EN 1540 [1].

3.1.4
exposure
⟨by inhalation⟩ situation in which a chemical agent is present in air which is inhaled by a person

3.1.5
measuring procedure
procedure for sampling and analysing one or more chemical agents in the air and including storage and transportation of the sample

3.1.6
operating time
period during which a sampling pump can be operated at specified flow rate and back pressure without recharging or replacing the battery

[EN 1232 [2]]

3.1.7
time-weighted average concentration
TWA concentration
concentration of a chemical agent in the atmosphere, averaged over the reference period

NOTE A more detailed discussion of TWA concentrations is available in Reference [3].

3.1.8
limit value
reference figure for concentration of a chemical agent in air

NOTE An example is the Threshold Limit Value® (TLV) for a given substance in workplace air, as established by the American Conference of Government Industrial Hygienists (ACGIH) [3].

3.1.9
reference period
specified period of time stated for the limit value of a specific chemical agent

NOTE Examples of limit values for different reference periods are short-term and long-term exposure limits, such as those established by the ACGIH [3].

3.1.10
workplace
defined area(s) in which the work activities are carried out

[EN 1540 [1]]

3.2 Particle size fraction definitions

3.2.1
inhalable convention
target specification for sampling instruments when the inhalable fraction is of interest

[ISO 7708]

3.2.2
inhalable fraction
mass fraction of total airborne particles which is inhaled through the nose and mouth

NOTE The inhalable fraction depends on the speed and direction of air movement, on breathing rate and other factors.

[ISO 7708]

3.2.3
respirable convention
target specification for sampling instruments when the respirable fraction is of interest

[ISO 7708]

3.2.4
respirable fraction
mass fraction of inhaled particles penetrating to the unciliated airways

[ISO 7708]

3.2.5
total airborne particles
all particles surrounded by air in a given volume of air

NOTE Because all measuring instruments are size-selective to some extent, it is often impossible to measure the concentration of total airborne particles.

[ISO 7708]

3.3 Sampling definitions

3.3.1
personal sampler
device attached to a person that samples air in the breathing zone

[EN 1540 [1]]

3.3.2
personal sampling
process of sampling carried out using a personal sampler

[EN 1540 [1]]

3.3.3
sampler
device for collecting airborne particles

NOTE Instruments used to collect airborne particles are frequently referred to by a number of other terms, e.g. sampling heads, filter holders, filter cassettes, etc.

3.3.4
static sampling
area sampling
process of air sampling carried out in a particular location

3.3.5
static sampler
area sampler
device, not attached to a person, used in static sampling

3.4 Analytical definitions

3.4.1
blank solution
solution prepared by taking a reagent blank, laboratory blank or field blank through the same procedure used for sample dissolution

3.4.2
calibration blank solution
calibration solution prepared without the addition of any working standard solution

NOTE The concentration of the analyte(s) of interest in the calibration blank solution is taken to be zero.

3.4.3
calibration solution
solution, prepared by dilution of the working standard solution, containing the analyte(s) of interest at a concentration that is suitable for use in calibration of the analytical instrument

3.4.4
field blank
filter that is taken through the same handling procedure as a sample, except that it is not used for sampling, but is loaded into a sampler, transported to the sampling site and then returned to the laboratory for analysis

3.4.5
laboratory blank
unused filter, taken from the same batch used for sampling, that does not leave the laboratory

3.4.6
linear dynamic range
range of concentrations over which the calibration curve for an analyte is linear

NOTE The linear dynamic range extends from the detection limit to the onset of calibration curvature.

3.4.7

reagent blank

all reagents used in sample dissolution, in the same quantities used for preparation of laboratory blank, field blank and sample solutions

3.4.8

sample dissolution

process of obtaining a solution containing all analytes on interest from a sample, which might or might not involve complete dissolution of the sample

3.4.9

sample preparation

all operations carried out on a sample, after transportation and storage, to prepare it for analysis, including transformation of the sample into a measurable state, if necessary

3.4.10

sample solution

solution prepared from a sample by the process of sample dissolution

NOTE A sample solution might need to be subjected to further operations, e.g. dilution, in order to produce a test solution that is ready for analysis.

3.4.11

test solution

blank solution or sample solution that has been subjected to all operations required to bring it into a state in which it is ready for analysis, e.g. dilution

NOTE The blank test solution is the blank solution and the sample test solution is the sample solution, if these solutions are not subjected to any further operations before analysis.

3.4.12

working standard solution

solution, prepared by dilution of the stock standard solution, that contains the analyte(s) of interest at a concentration(s) that is better suited to preparation of calibration solutions than the concentration(s) of the analyte(s) in the stock standard solution(s)

3.5 Statistical terms

3.5.1

analytical recovery

ratio of the mass of analyte measured in a sample when it is analysed to the known mass of analyte in that sample, expressed as a percentage

3.5.2

bias

consistent deviation of the results of a measurement process from the true value of the air quality characteristic itself

[ISO 6879 [4]]

3.5.3

overall uncertainty

⟨of a measuring procedure or of an instrument⟩ quantity used to characterise as a whole the uncertainty of a result given by an apparatus or measuring procedure

NOTE Uncertainty is expressed, as a percentage, by a combination of bias and precision, usually according to the formula:

$$\frac{\left|\bar{x} - x_{\text{ref}}\right| + 2s}{x_{\text{ref}}} \times 100$$

where

$\bar{x}$ is the mean value of results of a number (n) of repeated measurements;

x_{ref} is the true or accepted reference value of concentration;

s is the standard deviation of the measurements.

[EN 482 [5]]

3.5.4
precision
closeness of agreement of results obtained by applying the method several times under prescribed conditions

[ISO 6879 [4]]

3.5.5
true value
⟨of a quantity⟩ value which characterises a quantity perfectly defined in the conditions which exist when that quantity is considered

NOTE The true value of a quantity is a theoretical concept and, in general, cannot be known exactly.

[ISO 3534-1 [6]]

3.5.6
uncertainty of measurement
parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand

NOTE 1 The parameter might be, for example, a standard deviation (or a given multiple of it), or the width of a confidence interval.

NOTE 2 Uncertainty of measurement comprises, in general, many components. Some of these components can be evaluated from the statistical distribution of the results of series of measurements and can be characterised by standard deviations. The other components, which also can be characterised by standard deviations, are evaluated from assumed probability distributions based on experience or other information. The *Guide to the Expression of Uncertainty in Measurement* (GUM)[7] refers to these different cases as Type A and Type B evaluations of uncertainty, respectively.

NOTE 3 Adapted from the *International Vocabulary of Basic and General Terms in Metrology (VIM)* [8].

4 Principle

A known volume of air is drawn through a filter to collect airborne hexavalent chromium, using a sampler designed to collect the inhalable fraction of airborne particles (see 8.1.1).

The filter and collected sample are then treated to dissolve hexavalent chromium. Separate sample preparation methods are described for extraction of soluble and insoluble hexavalent chromium compounds, and either or both of these methods are used, as required, to prepare the sample for analysis. Soluble hexavalent chromium compounds are extracted with water or with ammonium sulfate/ammonium hydroxide solution, without heating. Insoluble hexavalent chromium compounds are extracted with sodium hydroxide ($\rho = 20\ \mathrm{g \cdot l^{-1}}$)/sodium carbonate solution ($\rho = 30\ \mathrm{g \cdot l^{-1}}$), either by heating on a hotplate or by ultrasonic extraction.

Aliquots of the sample solutions are analysed by ion chromatography in order to separate the extracted hexavalent chromium from trivalent chromium and other metal cations. Hexavalent chromium is measured spectrophotometrically at 540 nm after post-column derivatization with 1,5-diphenylcarbazide in acid solution.

Analytical results are obtained from plots of the measured absorbance as a function of concentration of hexavalent chromium. They can be used for assessment of occupational exposure to hexavalent chromium in air.

If desired, total hexavalent chromium can be measured directly using the sodium hydroxide/sodium carbonate extraction solution.

5 Reactions

Post-column derivatization involves reaction of hexavalent chromium with 1,5-diphenylcarbazide to produce trivalent chromium and diphenylcarbazone. These then combine to form a trivalent chromium-diphenylcarbazone complex containing the characteristic magenta chromagen (λ_{max} = 540 nm). However, the exact mechanism of this reaction is not fully understood.

6 Requirement

The measurement procedure shall comply with any relevant international, European or national standard which specifies performance requirements for procedures for measuring chemical agents in workplace air (e.g. EN 482 [5]).

7 Reagents

During the analysis, use only reagents of recognised analytical grade, and only water as specified in 7.1.

7.1 Water, complying with the requirements for ISO 3696 grade 2 water (electrical conductivity less than 0,1 mS·m^{-1} and resistivity greater than 0,01 MΩ·m at 25 °C).

It is recommended that the water used be obtained from a water purification system that delivers ultrapure water having a resistivity greater than 0,18 MΩ·m (usually expressed by manufacturers of water purification systems as 18 MΩ·cm).

7.2 Sulfuric acid (H_2SO_4), concentrated, $\rho \approx$ 1,84 g·ml^{-1}, mass fraction ≈ 98 %.

WARNING — Concentrated sulfuric acid is corrosive and causes burns. Avoid exposure by contact with the skin or eyes. Use suitable personal protective equipment (including suitable gloves, face shield or safety spectacles, etc.) when working with concentrated or dilute sulfuric acid. Fumes produced when concentrated sulfuric acid is heated are irritant. Therefore, carry out procedures with sulfuric acid in a fume hood. Exercise great caution when diluting sulfuric acid with water, since this process is very exothermic. Do not add water to sulfuric acid, since it reacts violently when mixed in this manner. Prepare sulfuric acid/water mixtures by adding sulfuric acid to water.

7.3 Nitric acid (HNO_3), concentrated, $\rho \approx$ 1,42 g·ml^{-1}, mass fraction ≈ 70 %.

WARNING — Concentrated nitric acid is corrosive and oxidizing, and nitric acid fumes are irritant. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Use suitable personal protective equipment (including suitable gloves, face shield or safety spectacles, etc.) when working with the concentrated or dilute nitric acid, and carry out procedures with concentrated nitric acid in open vessels in a fume hood.

7.4 Nitric acid, diluted 1 to 10.

Carefully and slowly add 50 ml of concentrated nitric acid (7.3) to 450 ml of water (7.1) in a 1-litre polypropylene bottle (8.2.3.1). Add the acid in small aliquots. Between additions, swirl to mix and run cold tap water over the side of the bottle to cool the contents. Do not allow tap water to contaminate the contents of the bottle. When addition of the concentrated nitric acid is complete, swirl the bottle to mix the contents, allow to cool to room temperature, close the bottle with its screw cap and mix thoroughly.

7.5 Ammonium sulfate [$(NH_4)_2SO_4$], mass fraction of ammonium sulfate $> 99{,}5$ %.

7.6 Ammonium hydroxide solution (NH_4OH), concentrated, $\rho \approx 0{,}9$ g·ml^{-1}, mass fraction ≈ 29 % of ammonia (NH_3).

WARNING — Concentrated ammonium hydroxide solution causes burns and is irritating to the respiratory system. Avoid exposure by contact with the skin or eyes, or by inhalation of the vapour. Use suitable personal protective equipment (including suitable gloves, face shield or safety spectacles, etc) when working with the concentrated ammonium hydroxide solution. Handle open vessels containing concentrated ammonium hydroxide solution in a fume hood.

7.7 Sodium carbonate (Na_2CO_3), anhydrous, mass fraction of sodium carbonate $> 99{,}9$ %.

7.8 Sodium hydroxide (NaOH), pellets, purity $> 99{,}5$ %.

WARNING — Sodium hydroxide causes burns and is irritating to the respiratory system. Avoid exposure by contact with the skin or eyes, or by inhalation of the dust. Use suitable personal protective equipment (including suitable gloves, face shield or safety spectacles, etc.) when working with the sodium hydroxide pellets or concentrated sodium hydroxide solutions.

7.9 1,5-Diphenylcarbazide ($(C_6H_5 \cdot NH \cdot NH)_2CO$), mass fraction of 1,5-diphenylcarbazide > 98 %.

7.10 Methanol (CH_3OH), HPLC grade.

7.11 Potassium dichromate ($K_2Cr_2O_7$), mass fraction of potassium dichromate $> 99{,}9$ %.

7.12 Extraction solutions

7.12.1 Soluble hexavalent chromium extraction solution concentrate, ammonium sulfate [$(NH_4)_2SO_4$], $c = 0{,}5$ mol·l^{-1}/ammonium hydroxide (NH_4OH), $c = 0{,}5$ mol·l^{-1}.

Dissolve 66 g of ammonium sulfate (7.5) in approximately 500 ml of water (7.1). Quantitatively transfer the solution into a 1-litre one-mark volumetric flask (8.2.2.2), add 32,5 ml of concentrated ammonium hydroxide (7.6) and swirl to mix. Dilute to the mark with water, stopper and mix thoroughly.

7.12.2 Soluble hexavalent chromium extraction solution, ammonium sulfate [$(NH_4)_2SO_4$], ($c = 0{,}05$ mol·l^{-1})/ammonium hydroxide (NH_4OH) ($c = 0{,}05$ mol·l^{-1}), pH 8.

Add 100 ml of soluble hexavalent chromium extraction solution concentrate (7.12.1) to a 1-litre one-mark volumetric flask (8.2.2.2), dilute to the mark with water (7.1), stopper and mix thoroughly.

Alternative extraction solutions at pH 8, e.g. $K_2HPO_4 \cdot 3\,H_2O$ ($\rho = 22{,}8$ g·l^{-1}) adjusted to pH 8 with orthophosphoric acid [9], may be used, if desired, provided that it can be demonstrated that the performance of the measuring procedure is not impaired.

7.12.3 Insoluble hexavalent chromium extraction solution, sodium hydroxide ($\rho = 20$ g·l^{-1})/sodium carbonate ($\rho = 30$ g·l^{-1}).

Dissolve 20 g of sodium hydroxide pellets (7.8) and 30 g of sodium carbonate (7.7) in 250 ml of water (7.1), swirl to mix and allow to cool. Quantitatively transfer the solution to a 1-litre volumetric flask (8.2.2.2), dilute to the mark with water, stopper and mix thoroughly.

Alternative extraction solutions, e.g. sodium carbonate ($\rho = 100$ g·l^{-1})/sodium hydrogen carbonate solution ($\rho = 20$ g·l^{-1}) [10], may be used if desired, provided it can be demonstrated that the performance of the measuring procedure is not impaired.

7.13 Eluent solutions

7.13.1 Eluent concentrate, ammonium sulfate $[(NH_4)_2SO_4]$ ($c = 2{,}0$ mol·l^{-1})/ammonium hydroxide (NH_4OH) ($c = 1$ mol·l^{-1}).

Dissolve 264 g of ammonium sulfate (7.5) in approximately 500 ml of water (7.1). Quantitatively transfer the solution into a 1-litre one-mark volumetric flask (8.2.2.2), add 65 ml of concentrated ammonium hydroxide (7.6) and swirl to mix. Dilute to the mark with water, stopper and mix thoroughly. Store in a polypropylene bottle (8.2.3.1) for a maximum period of one year.

7.13.2 Eluent solution, ammonium sulfate $[(NH_4)_2SO_4]$ ($c = 0{,}20$ mol·l^{-1})/ammonium hydroxide (NH_4OH) ($c = 0{,}1$ mol·l^{-1})

Add 100 ml of eluent concentrate (7.13.1) to a 1-litre one-mark volumetric flask (8.2.2.2), dilute to the mark with water (7.1), stopper and mix thoroughly.

7.14 pH indicator papers, suitable for measuring the pH of sample solutions (pH 8 ± 0,5) and the pH of effluent from the spectrophotometric detector (pH 2 or lower).

7.15 Hexavalent chromium standard solutions.

7.15.1 Hexavalent chromium stock standard solution.

a) Use a commercial standard solution with a certified hexavalent chromium concentration, e.g. $\rho = 1\,000$ mg·l^{-1}, traceable to national standards. Observe the manufacturer's expiration date or recommended shelf life.

   NOTE The concentration of commercial standard solutions is often expressed as milligrams per litre of chromate (CrO_4^{2-}) rather than milligrams per litre of hexavalent chromium. This needs to be taken into account when determining what volume of hexavalent chromium stock standard solution to use when preparing the hexavalent chromium working standard solution (7.15.2).

b) Alternatively, prepare a $\rho = 1\,000$ mg·l^{-1} hexavalent chromium stock standard solution by the following procedure.

   Dissolve 0,282 8 g of potassium dichromate (7.11) (previously dried to constant mass at 110 °C and cooled in a desiccator) in water (7.1). Quantitatively transfer the solution into a 100 ml one-mark volumetric flask (8.2.2.2), dilute to the mark with water, stopper and mix thoroughly. Store in a polypropylene bottle (8.2.3.1) for a maximum period of one year.

NOTE Potassium chromate (K_2CrO_4) can be used as an alternative to potassium dichromate for the preparation of a hexavalent chromium standard solution.

7.15.2 Hexavalent chromium working standard solution, $\rho = 10$ mg·l^{-1} of hexavalent chromium.

Accurately pipette an appropriate volume, e.g. 10,0 ml, of the hexavalent chromium stock standard solution (7.15.1) into a 1-litre one-mark volumetric flask (8.2.2.2), dilute to the mark with water (7.1), stopper and mix thoroughly. Prepare this solution fresh monthly.

7.16 Diphenylcarbazide reagent solution.

Add approximately 125 ml of water (7.1) to a 250 ml one-mark volumetric flask (8.2.2.2). Slowly and carefully add 7 ml of concentrated sulfuric acid (7.2), swirl to mix and allow to cool. Dissolve 0,125 g of 1,5-diphenylcarbazide (7.9) in 25 ml of methanol (7.10), quantitatively transfer the resulting solution into the volumetric flask, dilute to the mark with water (7.1), stopper and mix thoroughly. Prepare this solution fresh daily.

Other suitable solvents (e.g. acetone) may be used for preparation of the 1,5-diphenylcarbazide solution, if desired.

8 Apparatus

8.1 Sampling equipment

8.1.1 Samplers, designed to collect the inhalable fraction of airborne particles, complying with EN 13205.

The operating instructions supplied by the manufacturer of any sampling cassette should be consulted to find out whether particulate matter deposited on the internal surfaces of the sampler forms part of the sample.

NOTE 1 In general, personal samplers for collection of the inhalable fraction of airborne particles do not exhibit the same size-selective characteristics if used for static sampling.

NOTE 2 Some inhalable samplers are designed to collect the inhalable fraction of airborne particles on the filter, so that any particulate matter deposited on the internal surfaces of the sampler is not of interest. Other inhalable samplers are designed such that airborne particles which pass through the entry orifice(s) match the inhalable convention, in which case particulate matter deposited on the internal surfaces of the sampler does form part of the sample. (Samplers of this second type generally incorporate an internal filter cassette or cartridge that can be removed from the sampler to enable this material to be easily recovered.)

8.1.2 Filters, of a diameter suitable for use with the samplers (8.1.1), with a collection efficiency of not less than 99,5 % for particles with a 0,3 µm diffusion diameter (see ISO 7708:1995, 2.2), manufactured from a material that does not react with hexavalent chromium and that is compatible with the sample preparation and analysis method.

Hexavalent chromium is a powerful oxidizing agent. It reacts with many organic and polymeric materials, and in the process is reduced to the trivalent state. Consequently, correct selection of the filter used for sample collection is of paramount importance. In particular, the filter should be manufactured from a material that does not react with hexavalent chromium. The following filters are generally suitable for use:

- polyvinyl chloride (PVC) membrane filters, pore size 5 µm or less;
- polyvinyl fluoride (PVF) membrane filters, pore size 5 µm or less;
- polytetrafluoroethylene (PTFE) membrane filters, pore size 5 µm or less;
- PVC/acrylic copolymer membrane filters, pore size 5 µm or less; and
- quartz-fibre filters.

Cellulose-based filters and glass-fibre filters with a binder are generally unsuitable, as their use can lead to significant reduction of hexavalent chromium. Certain types of PVC filter have also been reported to cause hexavalent chromium reduction [10], and this should be investigated prior to their use.

NOTE When sampling chromic acid mist, there is an advantage if the oxidizing potential of hexavalent chromium is lowered by impregnating the filter with alkali, for example by soaking the filters overnight in 1 mol/l sodium hydroxide and allowing to dry in a clean environment [11]. This lessens the tendency of hexavalent chromium to react with organic compounds in the filter material and/or with reducing agents and dust present in the sampled air. It also improves sample stability. Filter materials such as PVC and PTFE can be unsuitable for alkali treatment, since they can be hydrophobic and therefore not easily wetted. Membrane filters of polyvinylidine fluoride and of vinyl/acrylic copolymer have been found to be suitable for alkali treatment.

8.1.3 Back-up pads, if necessary, for use with the samplers (8.1.1).

Cellulose back-up pads should be used with caution when sampling chromic acid mist, since droplets can penetrate the filter by capillary force and then be reduced by reaction with the back-up pad material. A glass- or quartz-fibre back-up pad could be used, or a mesh made of chromic acid-resistant material.

8.1.4 Sampling pumps, with an adjustable flow rate, capable of maintaining the selected flow rate (see 10.1.1.2) to within ± 5 % of the nominal value throughout the sampling period (see 10.1.2).

For personal sampling, the pumps shall be capable of being worn by the worker without impeding normal work activity. Sampling pump flowmeters shall be calibrated using either a primary or secondary standard; if a secondary standard is used, it shall be calibrated using a primary standard.

The pump should have, as a minimum, the following features:

- an automatic control that keeps the volumetric flow rate constant in the case of a changing back pressure;
- either a malfunction indicator which, following completion of sampling, indicates that the air flow has been reduced or interrupted during sampling; or an automatic cut-out, which stops the pump if the flow rate is reduced or interrupted, and
- a facility for the adjustment of flow rate, such that it can only be actuated with the aid of a tool (e.g. screwdriver) or requires special knowledge for operation (e.g. via software), so as to preclude inadvertent readjustment of the flow rate during use.

An integral timer is a highly desirable additional feature.

NOTE 1 A flow-stabilized pump may be required to maintain the flow rate within the specified limits.

NOTE 2 EN 1232 [2] and EN 12919 [12] require that the performance of the pumps be such that

- the pulsation of the flow rate does not exceed 10 %,
- a flow rate set within the nominal range does not deviate by more than ± 5 % from the initial value under increasing back-pressure,
- within the range of ambient temperatures from 5 °C to 40 °C, the flow rate measured under operating conditions does not deviate by more than ± 5 % from the flow rate at 20 °C,
- the operating time is at least 2 h and preferably 8 h, and
- the flow rate does not deviate by more than ± 5 % from the initial value during the operating time.

If the sampling pump is used outside the range of conditions specified in EN 1232 [2] and/or EN 12919 [12], appropriate action should be taken to ensure that the performance requirements are met. For instance, at sub-zero temperatures it might be necessary to keep the pump warm.

8.1.5 Flowmeter, portable, with an accuracy that is sufficient to enable the volumetric flow rate (see 10.1.1.2) to be measured to within ± 5 %.

The calibration of the flowmeter shall be checked against a primary standard, i.e. a flowmeter whose accuracy is traceable to national standards. If appropriate (see 10.1.3), the atmospheric temperature and pressure at which the calibration of the flowmeter was checked shall be recorded.

It is advisable to use a flowmeter that is capable of measuring the volumetric flow rate to within ± 2 % or better.

8.1.6 Ancillary equipment

8.1.6.1 Flexible tubing, of a diameter suitable for making a leakproof connection from the samplers (8.1.1) to the sampling pumps (8.1.4).

8.1.6.2 Belts or **harnesses**, to which the sampling pumps can conveniently be fixed for personal sampling (except where the sampling pumps are small enough to fit in workers' pockets).

8.1.6.3 Flat-tipped forceps, non-metallic (e.g. plastic or PTFE-coated), for loading and unloading filters into samplers.

8.1.6.4 Filter transport cassettes or similar, if required (see 10.5.1), in which to transport samples to the laboratory.

Filter transport cassettes should be not made of material that contains residual plasticisers that could be released during transport and storage, as plasticisers can cause reduction of hexavalent chromium.

8.1.6.5 Thermometer, reading 0 °C to 50 °C, graduated in divisions of 1 °C or better, for measurement of atmospheric temperature, if required (see 10.1.3). For applications at temperatures below freezing, the range of the thermometer shall extend to the appropriate desired range.

8.1.6.6 Barometer, suitable for measurement of atmospheric pressure, if required (see 10.1.3).

8.2 Laboratory apparatus

Ordinary laboratory apparatus, and the following.

8.2.1 Disposable gloves, impermeable, to avoid the possibility of contamination from the hands and to protect them from contact with toxic and corrosive substances. PVC gloves are suitable.

8.2.2 Glassware, made of borosilicate glass 3.3 complying with the requirements of ISO 3585, cleaned before use by soaking in nitric acid (7.4) for at least 24 h and then rinsing thoroughly with water (7.1).

Alternatively, the glassware may be cleaned with a suitable laboratory detergent using a laboratory washing machine.

Under no circumstances should chromic acid be used to clean glassware.

8.2.2.1 Beakers, of capacities between 100 ml and 2 litres, for preparation of the extraction solutions (7.12) and the eluent concentrate (7.13.1), the hexavalent chromium stock solution (7.15.1.2) and the 1,5-diphenylcarbazide solution (7.16); and of capacities between 50 ml and 150 ml, of a form compatible with filters of the diameter used in the sampler (see 8.1.2), with watch glasses to fit, for preparation of test solutions.

8.2.2.2 One-mark volumetric flasks, of capacities between 10 ml and 1 000 ml, complying with the requirements of ISO 1042.

8.2.2.3 One-mark pipettes, complying with ISO 648.

8.2.3 Plasticsware

8.2.3.1 Polypropylene bottles, of capacities between 100 ml and 1 000 ml.

8.2.3.2 Polypropylene tubes, disposable, graduated, of capacity between 10 ml and 30 ml, with push-fit closures or screw caps.

NOTE Tubes without graduation are acceptable if test solutions are made up in volumetric flasks.

8.2.3.3 Filter funnels, of a size suitable for use in transferring washings from the internal surfaces of the sampler (see 11.3.3.2) into a tube (8.2.3.2).

8.2.4 Piston-operated volumetric instruments, complying with ISO 8655-1, and tested in accordance with ISO 8655-6, as follows.

8.2.4.1 Piston pipettes, complying with ISO 8655-2, as an alternative to one-mark pipettes for the preparation of standard solutions, calibration solutions and dilution of samples.

8.2.4.2 Dispensers, complying with ISO 8655-5, for dispensing acids.

8.2.5 Hotplate, thermostatically controlled, capable of maintaining a surface temperature of approximately 135 °C, suitable for use in the hotplate extraction method for insoluble hexavalent chromium compounds (11.3.2).

8.2.6 Suction filtration equipment

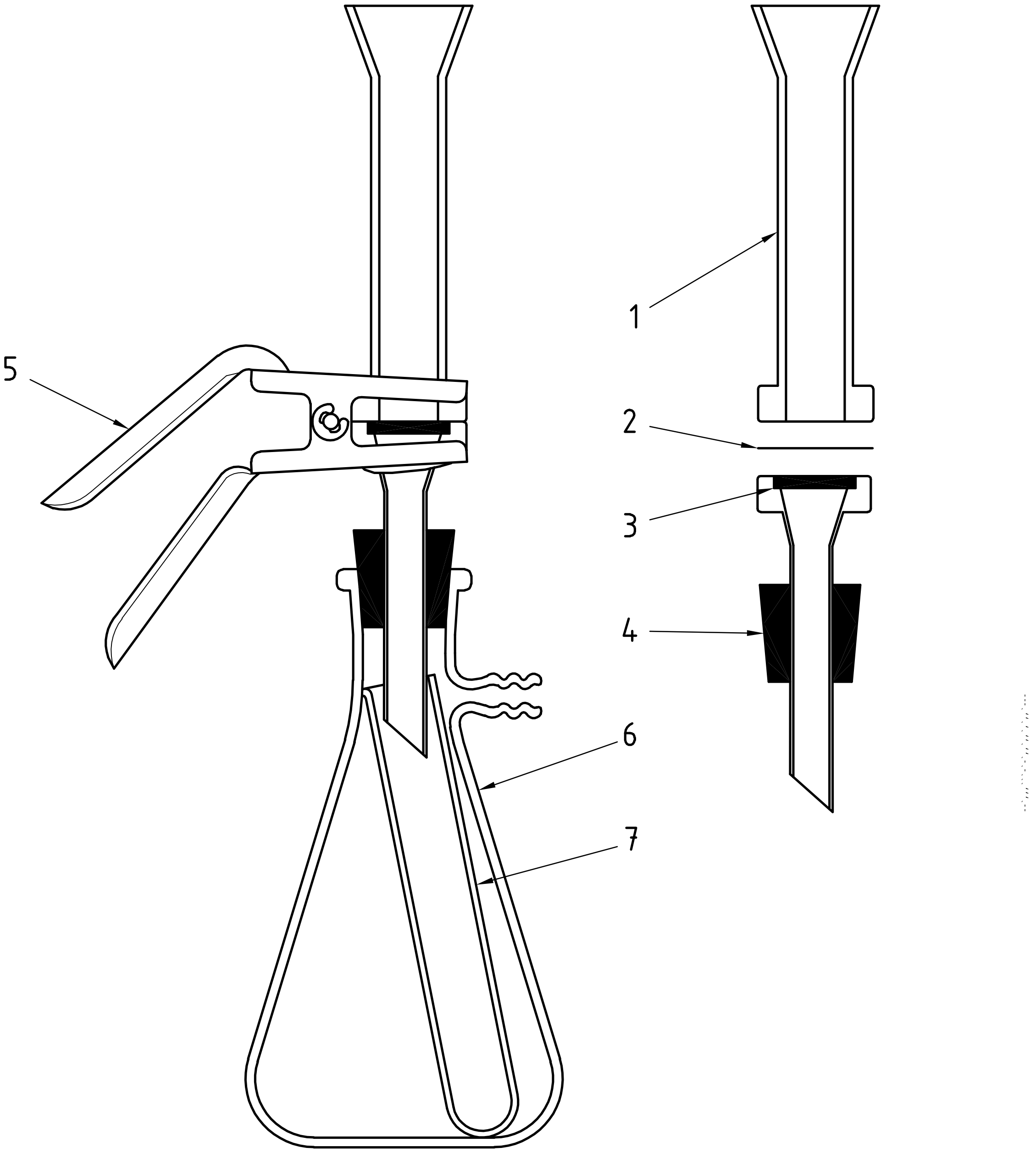
8.2.6.1 Suction filtration apparatus, typically a water-operated or electrically driven vacuum pump, connected to a conical flask fitted with a filter funnel/support assembly (see Figure 1).

NOTE Alternative suction filtration apparatus is commercially available that permits simultaneous vacuum filtration of multiple sample solutions.

8.2.6.2 Membrane filters, chemically inert, of a diameter suitable for use with the suction filtration apparatus (8.2.6.1).

8.2.7 Ultrasonic bath, preferably with a timer, suitable for use in the ultrasonic extraction method for insoluble hexavalent chromium compounds (11.3.3).

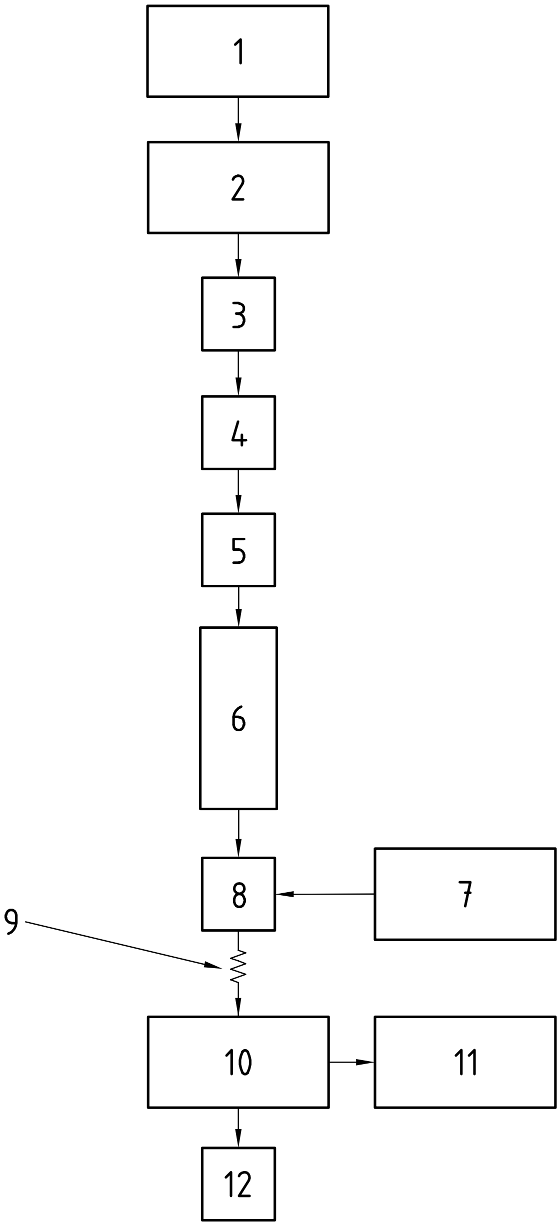
8.2.8 Ion chromatograph, having the following components listed in 8.2.8.1 through 8.2.8.9 and shown in Figure 2. All components which come into contact with the sample or eluent stream shall, to the extent possible, be comprised of inert materials, e.g. poly(ether ether ketone) (PEEK), as shall all connecting tubing.



Key

1 filter funnel
2 membrane filter
3 fritted glass base
4 stopper
5 spring clamp
6 filtering flask, 250 ml
7 tube, 16 mm × 95 mm

Figure 1 — Example of a suction filtration apparatus



Key

1	eluent reservoir
2	pump
3	injection valve
4	sample loop
5	guard column
6	separator column
7	reagent delivery module
8	mixing tee
9	reaction coil
10	spectrophotometric detector
11	data handling system
12	waste

Figure 2 — Diagrammatic representation of an ion chromatography system configured for post-column derivatization and spectrophotometric detection

8.2.8.1 **Pump**, capable of delivering a constant flowrate within the range 1 ml·min^{-1} to 5 ml·min^{-1} at a pressure of 15 MPa to 150 MPa.

8.2.8.2 **Sample injection system**

Either

8.2.8.2.1 **Autosampler**, with all components coming in contact with the sample solution made of non-metallic material.

or

8.2.8.2.2 **Manual sample injection system**, comprising a low dead-volume, non-metallic valve fitted with a sample loop having a volume of up to 1 ml, for injecting the sample solution into the eluent stream; together with a compatible metal-free injection syringe.

8.2.8.3 **Guard column**, placed before the separator column (8.2.8.4) to protect the separator column from fouling by particles or strongly adsorbed organic constituents.

8.2.8.4 **Separator column**, packed with high capacity pellicular anion-exchange resin that is suitable for resolving hexavalent chromium from other metals and cations.

8.2.8.5 **Reagent delivery module**, capable of delivering 0,1 ml·min^{-1} to 2,0 ml·min^{-1} of reagent solution against a back-pressure of up to 40 kPa.

8.2.8.6 **Mixing tee** and **reaction coil**, capable of mixing two flowing streams with minimal band spreading.

8.2.8.7 **Absorbance detecto**r, flow-through, low volume, with a non-metallic flow path, suitable for measuring absorbance at 540 nm.

8.2.8.8 **Recorder**, integrator or computer, compatible with detector output, capable of recording detector response as a function of time, for the purpose of measuring peak height or area. The use of an automated system is recommended.

8.2.8.9 **Eluent reservoir**, comprising a container suitable for storing eluent.

8.2.9 **pH meter**, suitable for measuring the pH of sample solutions and of effluent from the spectrophotometric detector.

9 Occupational exposure assessment

9.1 General

This International Standard pertains to the taking of personal and static samples. See relevant international, european or national standards (e.g. EN 689 [13], ASTM E 1370-96 [14], etc.) for guidance on how to develop an appropriate assessment strategy and for general guidance on measurement strategy.

9.2 Personal sampling

Exposure of workers to hexavalent chromium shall normally be determined by personal sampling, since the concentration of hexavalent chromium in the breathing zone can be different from the background level in the workplace.

9.3 Static sampling

Static sampling may be carried out, if appropriate, to assess the exposure of workers in a situation where personal sampling is not possible (see Note in 10.1.2.1 for an example of such a situation); to characterise the background level of hexavalent chromium in the workplace in order to give an indication of the efficiency of ventilation; or to provide information on the location and intensity of an emission source.

9.4 Selection of measurement conditions and measurement pattern

9.4.1 General

9.4.1.1 Sampling shall be carried out in such a way as to cause the least possible interference with the worker and the normal performance of the job, and to provide samples that are representative of normal working conditions and that are compatible with the analytical method.

9.4.1.2 The pattern of sampling shall take into consideration practical issues, such as the nature of the measurement task and the frequency and duration of particular work activities.

9.4.2 Screening measurements of variation of concentration in time and/or space

Screening measurements of variation of concentration in time and/or space may be performed to provide information on the likely pattern of concentration of chemical agents. They can be used to identify locations and periods of elevated exposure and to set the duration and frequency of sampling for measurements for comparison with limit values. Emission sources can be located and the effectiveness of ventilation or other technical measures can be estimated (see 4.3 of EN 482:1994 [5]).

9.4.3 Screening measurements of time-weighted average concentration and worst-case measurements

9.4.3.1 Screening measurements of time-weighted average concentration may be performed to obtain relatively crude information on the exposure level in order to decide whether an exposure problem exists at all, and if so to appraise its possible seriousness. They may also be used to determine if the exposure is well below or well above the limit value (see 4.2 of EN 482:1994 [5]).

9.4.3.2 Screening measurements of time-weighted average concentration are typically carried out in the initial stages of a survey to assess the effectiveness of control measures. Sampling may be carried out during representative work episodes to obtain clear information about the level and pattern of exposure, or worst case measurements may be made.

NOTE Screening measurements of time-weighted average concentration made to clearly identify work episodes during which highest exposure occurs are typically referred to as "worst-case measurements" (see 5.2.3.2 of EN 689:1995 [13]).

9.4.4 Measurements near an emission source

Measurements may be performed near an emission source to provide information on the location and intensity of the source. In association with other information, they can allow the elimination of a suspected source as a significant contributor to exposure (see 4.4 of EN 482:1994 [5]).

9.4.5 Measurements for comparison with limit values and periodic measurements

9.4.5.1 Measurements for comparison with limit values

9.4.5.1.1 Measurements for comparison with limit values are performed to provide accurate and reliable information on, or allow the prediction of, the time-weighted average concentration of a specific chemical agent in the air that could be inhaled. (see 4.5 of EN 482:1994 [5]).

9.4.5.1.2 For making measurements for comparison with a short-term exposure limit, the sampling time shall be as close as possible to the reference period, which is typically 15 min, but can be anything between 5 min and 30 min.

9.4.5.1.3 For making measurements for comparison with a long-term exposure limit, samples shall be collected for the entire working period, if possible, or during a number of representative work episodes throughout the working period (see 10.1.2.1 for the minimum sampling time).

NOTE The best estimate of long-term exposure is obtained by taking samples for the entire working period, but this is often not practicable (e.g. because of the possibility of overloading the filter).

9.4.5.2 Periodic measurements

Periodic measurements are performed to determine whether exposure conditions have changed since measurements for comparison with limit values were made, or whether control measures remain effective (see 4.6 of EN 482:1994 [5]).

10 Sampling method

10.1 Preliminary considerations

10.1.1 Selection and use of samplers

10.1.1.1 Select samplers (8.1.1) designed to collect the inhalable fraction of airborne particles, as defined in ISO 7708.

If possible, the samplers selected should be manufactured from conducting material, since samplers manufactured from non-conducting material have electrostatic properties, which can influence representative sampling.

NOTE The results of a collaborative study of personal inhalable aerosol sampler performance [15] provide information that could be of use when selecting samplers.

10.1.1.2 Use the samplers at their design flow rate and in accordance with the instructions provided by the manufacturer, so that they collect the inhalable fraction of airborne particles.

10.1.2 Sampling period

10.1.2.1 Select a sampling period that is appropriate for the measurement task (see 9.4), but ensure that it is long enough to enable hexavalent chromium to be determined with acceptable overall uncertainty at levels of industrial hygiene significance. For example, estimate the minimum sampling time required to ensure that the amount collected is above the lower limit of the working range of the analytical method when hexavalent chromium is present in the test atmosphere at a concentration of 0,1 times its limit value, using the following equation:

$$t_{\text{min}} = \frac{m_{\text{lower}}}{q_V \times 0{,}1 \times \rho_{\text{LV}}} \tag{1}$$

where

t_{min} is the minimum sampling time, in minutes;

m_{lower} is the lower limit of the analytical range, in micrograms;

q_V is design flow rate of the sampler, in litres per minute;

ρ_{LV} is the limit value, in milligrams per cubic metre.

NOTE If the minimum sampling time is not short enough for the method to be useful for the intended measurement task, consider the possibility of using a sampler designed to be used at a higher flow rate. This might require using a static sampler if the design flow rate of available personal samplers is too low (see 10.3.2.1).

10.1.2.2 When high concentrations of airborne particles are anticipated, select a sampling period that is not so long as to risk overloading the filter with particulate matter.

10.1.3 Temperature and pressure effects

10.1.3.1 Effect of temperature and pressure on flow rate measurements

Refer to the manufacturer's instructions to determine if the indicated volumetric flow rate of the flowmeter (8.1.5) is dependent upon temperature and pressure. Consider whether the difference between the atmospheric temperature and pressure at the time of calibration of the flowmeter and at the time of sampling is likely to be great enough to justify making a correction to take this into account, e.g. if the error could be greater than ± 5 %. If a correction is necessary, measure and record the atmospheric temperature and pressure at which the calibration of the flowmeter is checked (see 8.1.5), and measure and record the atmospheric temperature and pressure at the start and at the end of the sampling period (see 10.4.1 and 10.4.3).

NOTE An example of temperature and pressure corrections for the indicated volumetric flow rate is given in A.1 for a constant pressure drop, variable area, flowmeter.

10.1.3.2 Expression of results

Consider whether it is necessary to recalculate the concentration of hexavalent chromium in air to reference conditions (see ISO 8756[16]). If so, measure and record the atmospheric temperature and pressure at the start and at the end of the sampling period (see 10.4.1 and 10.4.3) and use Equation (A.2) to apply the necessary correction.

NOTE The concentration of hexavalent chromium in air is generally stated for actual environmental conditions (temperature, pressure) at the workplace.

10.1.4 Handling of filters

To minimise the risk of damage or contamination, only handle filters using flat-tipped forceps (8.1.6.3), in a clean area, where the concentration of hexavalent chromium is as low as possible.

10.2 Preparation for sampling

10.2.1 Cleaning of samplers

Unless disposable filter cassettes are used, clean the samplers (8.1.1) before use. Disassemble the samplers, soak in detergent solution, rinse thoroughly with water, wipe with absorbent tissue and allow to dry before reassembly.

Alternatively, use a laboratory washing machine.

10.2.2 Loading the samplers with filters

Load clean samplers (see 10.2.1) with filters (8.1.2), label each sampler so that it can be uniquely identified, and seal with its protective cover or plug to prevent contamination.

Alternatively, commercially available pre-loaded filter cassettes may be used.

10.2.3 Setting the volumetric flow rate

Perform the following in a clean area, where the concentration of hexavalent chromium is as low as possible:

Connect each loaded sampler (see 10.2.2) to a sampling pump (8.1.4) using flexible tubing (8.1.6.1), ensuring that no leaks can occur. Remove the protective cover or plug from each sampler, switch on the sampling pump, attach the flowmeter (8.1.5) to the sampler so that it measures the flow through the sampler inlet orifice(s), and set the required volumetric flow rate (see 10.1.1.2). Switch off the sampling pump and seal the sampler with its protective cover or plug to prevent contamination during transport to the sampling location.

If necessary, allow the sampling-pump operating conditions to stabilize before setting the volumetric flow rate.

10.2.4 Field blanks

Retain as field blanks, at least one unused loaded sampler from each batch of ten prepared, subject to a minimum of three. Treat these in the same manner as those used for sampling in respect of storage and transport to and from the sampling location, but draw no air through the filters.

10.3 Sampling position

10.3.1 Personal sampling

10.3.1.1 Position the sampler in the worker's breathing zone, as close to the mouth and nose as is reasonably practicable, e.g. fastened to the worker's shirt collar or lapel. Attach the sampling pump to the worker in a manner that causes minimum inconvenience, e.g. to a belt (8.1.6.2) around the waist, or place it in a convenient pocket.

10.3.1.2 Give consideration to whether the nature of the process is likely to result in a significant difference between the actual exposure of the worker and the concentration of hexavalent chromium measured by a sampler mounted on the shirt collar or lapel. If this is the case, make special arrangements to mount the sampler as close as possible to the worker's nose and mouth.

NOTE An example of the need to make special arrangements to mount the sampler as close as possible to the worker's nose and mouth is in welding and allied processes, when the use of a welder's face shield provides a degree of protection by physically deflecting the plume of welding fume away from the breathing zone, and sampling on the shirt collar or lapel could overestimate exposure (see ISO 10882-1 [17]).

10.3.2 Static sampling

10.3.2.1 If static sampling is carried out to assess the exposure of a worker in a situation where personal sampling is not possible (e.g. due to the need to sample at a volumetric flow rate higher than the design flow rate of available personal samplers), position the sampler in the immediate vicinity of the worker and at breathing height. If in doubt, take the sampling to be the point where the risk of exposure is considered to be greatest.

10.3.2.2 If static sampling is carried out to characterise the background level of hexavalent chromium in the workplace, select a sampling position that is sufficiently remote from the work processes, such that results will not be directly affected by hexavalent chromium from emission sources.

10.3.2.3 If static sampling is carried out to measure hexavalent chromium emission, select a suitable sampling position near the emission source.

10.4 Collection of samples

10.4.1 When ready to begin sampling, remove the protective cover or plug from the sampler and switch on the sampling pump. If the sampling pump is fitted with an integral timer, check that this is reset to zero prior to turning it on. Record the time and volumetric flow rate at the start of the sampling period. If appropriate (see 10.1.3), measure the atmospheric temperature and pressure at the start of the sampling period using the thermometer (8.1.6.5) and barometer (8.1.6.6), and record the measured values.

Integral timers built into sampling pumps can be imprecise and should only be used to provide evidence that the sampler has been operating properly throughout the sampling period (see 10.4.3).

NOTE If the temperature or pressure at the sampling position is different from that where the volumetric flow rate was set (see 10.2.3), the volumetric flow rate could change and it might need to be re-adjusted before sampling.

10.4.2 Monitor the performance of the pumps frequently, a minimum of once every 2 h. Measure the flow rate using the flowmeter (8.1.5) and record the measured value. Terminate sampling and consider the sample to be invalid if the flow rate is not maintained to within ± 5 % of the nominal value throughout the sampling period.

10.4.3 At the end of the sampling period (see 10.1.2), record the time and calculate the duration of the sampling period. Check the malfunction indicator and/or the reading on the integral timer, if fitted, and consider the sample to be invalid if there is evidence that the sampling pump was not operating properly throughout the sampling period. Measure the volumetric flow rate at the end of the sampling period using the flowmeter (8.1.5), and record the measured value. If appropriate (see 10.1.3), measure the atmospheric temperature and pressure at the end of the sampling period using the thermometer (8.1.6.5) and barometer (8.1.6.6), and record the measured values.

10.4.4 Carefully record the sample identity and all relevant sampling data (see Clause 15). Calculate the mean volumetric flow rate by averaging the volumetric flow rates at the start and at the end of the sampling period and, if appropriate (see 10.1.3), calculate the mean atmospheric temperature and pressure. Calculate the volume of air sampled, in litres, at atmospheric temperature and pressure, by multiplying the mean flow rate, in litres per minute, by the duration of the sampling period, in minutes.

10.5 Transportation

10.5.1 For samplers which collect airborne particles on the filter (see Note 2 in 8.1.1), remove the filter from each sampler, place in a labelled filter transport cassette (8.1.6.4) and close with a lid. Take particular care to prevent the collected sample from becoming dislodged from heavily loaded filters.

Alternatively, transport samples to the laboratory in the samplers in which they were collected.

10.5.2 For samplers which have an internal filter cassette (see Note 2 in 8.1.1), remove the filter cassette from each sampler and fasten with its lid or transport clip.

10.5.3 For samplers of the disposable cassette type, transport samples to the laboratory in the samplers in which they were collected.

10.5.4 Transport the samples (10.5.1 through 10.5.3) to the laboratory in a container which has been designed to prevent damage to the samples in transit and which has been labelled to assure proper handling.

10.5.5 Ensure that the documentation which accompanies the samples is suitable for a "chain of custody" to be established (see, for example, ASTM D 4840-01 [18]).

10.5.6 Follow the same procedure for the field blanks (10.2.4).

10.5.7 Analyse the samples as soon as possible after sampling.

11 Analysis

CAUTION — Perform all operations involving hexavalent chromium while wearing gloves.

11.1 Analytical requirements

11.1.1 Selection criteria

Decide whether it is necessary to determine soluble hexavalent chromium compounds, insoluble hexavalent chromium compounds or both, taking into consideration the applicable national exposure limits and the nature of the hexavalent chromium-containing material present in the test atmosphere. Follow the instructions given in 11.1.2 through 11.1.6.

11.1.2 Measurements for comparison with a limit value for soluble hexavalent chromium compounds

If results are required for comparison with a limit value for soluble hexavalent chromium compounds, and it is known that only soluble hexavalent chromium compounds are present in the test atmosphere, use the sample preparation method specified in 11.2 to prepare the test solutions.

11.1.3 Measurements for comparison with a limit value for insoluble hexavalent chromium compounds

11.1.3.1 If the results are required for comparison with a limit value for insoluble hexavalent chromium compounds, and it is known that no soluble hexavalent chromium compounds are present in the test atmosphere, use one of the sample dissolution methods specified in 11.3 to prepare the test solutions.

11.1.3.2 If the results are required for comparison with a limit value for insoluble hexavalent chromium compounds, and both soluble and insoluble hexavalent chromium compounds could be present in the test atmosphere, follow the instructions given in 11.1.4, but discard the test solutions prepared for determination of soluble hexavalent chromium compounds.

11.1.4 Measurements for comparison with a limit value for soluble hexavalent chromium compounds and with a limit value for insoluble hexavalent chromium compounds

If results are required for comparison with separate limit values for soluble and insoluble hexavalent chromium compounds, and both could be present in the test atmosphere, then:

- use the sample dissolution method specified in 11.2 to prepare test solutions for determination of soluble hexavalent chromium compounds; and
- use one of the sample dissolution methods specified in 11.3 to treat undissolved material from the method for soluble hexavalent chromium compounds and prepare test solutions for determination of insoluble hexavalent chromium compounds.

11.1.5 Measurements for comparison with a limit value for soluble hexavalent chromium compounds and with a limit value for total hexavalent chromium compounds

If results are required for comparison with separate limit values for soluble and total hexavalent chromium compounds, and both soluble and insoluble hexavalent chromium compounds could be present in the test atmosphere, then:

- use the sample dissolution method specified in 11.2 to prepare test solutions for determination of soluble hexavalent chromium compounds;
- use one of the sample dissolution methods specified in 11.3 to treat undissolved material from the method for soluble hexavalent chromium compounds and prepare test solutions for determination of insoluble hexavalent chromium compounds; and

- add the results obtained for soluble hexavalent chromium compounds to those obtained for insoluble hexavalent chromium compounds in order to calculate results for total hexavalent chromium compounds.

11.1.6 Measurements for comparison with a limit value for total hexavalent chromium compounds

If the results are required for comparison with a limit value for total hexavalent chromium compounds, and separate national exposure limits for soluble and insoluble hexavalent chromium compounds do not exist, either use one of the sample preparation methods for insoluble hexavalent chromium compounds specified in 11.3 to prepare test solutions or, if is known that only soluble hexavalent chromium compounds are present in the test atmosphere, use the sample preparation method specified in 11.2 to prepare the test solutions.

11.2 Preparation of solutions for determination of soluble hexavalent chromium compounds

11.2.1 Selection of sample preparation method for soluble hexavalent chromium compounds

Decide whether to use water (7.1) or soluble hexavalent chromium extraction solution (7.12.2) to prepare test solutions for determination of soluble hexavalent chromium compounds. See B.1.5 and B.2.2 for guidance.

NOTE Useful background information on methods for determination of soluble hexavalent chromium compounds in air and guidance on their use is given in Annex B. Further guidance can be found in a recently published critical review paper [19] on this topic.

11.2.2 Preparation of blank and sample test solutions

11.2.2.1 The following procedure may be carried out using laboratory plasticsware instead of glass beakers.

11.2.2.2 Open the filter transport cassettes, sampler filter cassettes or samplers (see 10.5) and transfer each filter into an individual labelled 50 ml beaker (8.2.2.1) using clean flat-tipped forceps (8.1.6.3).

Accurately pipette 5 ml of water (7.1) or soluble hexavalent chromium extraction solution (7.12.2) into each beaker. If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the sampler form part of the sample (see Note 2 in 8.1.1), use the water or extraction solution to carefully wash any particulate material adhering to the internal surfaces of the sampler into the beaker.

The dissolution may be carried out in the sampler, if it is watertight when the air inlet and outlet orifices are sealed with their protective plugs, and if it is of sufficient capacity (see Reference [20]). In this case, water or extraction solution should be added to each sampler via the air-inlet orifice, and the samplers should be positioned in the water bath in a suitable manner, so that spillage and contamination of the sample solutions is avoided.

11.2.2.3 Cover each beaker with a watch glass and swirl gently to mix the contents, ensuring that the filter remains completely immersed.

11.2.2.4 Allow the immersed filters to sit for 1 h at room temperature, swirling or agitating occasionally. Do not use ultrasonic agitation to promote sample dissolution.

11.2.2.5 Filter each solution through a membrane filter (8.2.6.2) using suction filtration apparatus (8.2.6.1), collecting the filtrate in an individual, labelled, 10 ml tube (8.2.3.2).

If the extraction was carried out in the sampler, the blank or sample filter may be used to filter the solution. This can be achieved by using flexible plastic tubing to connect the air outlet orifice of the sampler directly to the suction filtration apparatus, having substituted the filter funnel/support assembly with a short length of glass or plastic tubing.

Alternatively, centrifugation or syringe filters may be used to remove undissolved material unless it is to be retained for subsequent determination of insoluble hexavalent chromium compounds (see 11.2.2.9).

11.2.2.6 Rinse each blank and sample filter and its associated beaker with two 1 ml aliquots of water (7.1) or soluble hexavalent chromium extraction solution (7.12.2), according to which was used for extraction, allowing the liquid to completely drain from the filter funnels between washings.

11.2.2.7 If water (7.1) was used in 11.2.2.2, either

a) add 1 ml of soluble hexavalent extraction solution concentrate (7.12.1) to each blank and sample solution (11.2.2.6) and dilute to the 10 ml graduation of the tube with water (7.1). Seal each tube with its screw cap or push-fit closure and mix thoroughly to produce the test solution,

or

b) quantitatively transfer each blank and sample solution (11.2.2.6) to an individual, labelled, 10 ml volumetric flask (8.2.2.2) to which 1 ml of soluble hexavalent extraction solution concentrate (7.12.1) has been added, rinsing out the test tube and diluting to the mark with water (7.1). Stopper and mix thoroughly to produce the test solution.

11.2.2.8 If soluble hexavalent extraction solution (7.12.2) was used in 11.2.2.2, either

a) dilute each blank and sample solution (11.2.2.6) to the 10 ml graduation of the test tube with soluble hexavalent chromium extraction solution (7.12.2). Seal each tube with its screw cap or push-fit closure and mix thoroughly to produce the test solution,

or

b) quantitatively transfer each blank and sample solution (11.2.2.6) to an individual, labelled, 10 ml volumetric flask (8.2.2.2), rinsing out the test tube and diluting to the mark with soluble hexavalent extraction solution (7.12.2). Stopper and mix thoroughly to produce the test solution.

11.2.2.9 If test solutions are also to be prepared for determination of insoluble hexavalent chromium compounds (see 11.1.4 and 11.1.5), retain for subsequent analysis both the extracted blank and sample filters and the secondary filters used to remove undissolved material from the soluble hexavalent chromium sample solution.

11.2.3 Preparation of calibration solutions

Prepare a minimum of six calibration solutions, including a calibration blank solution, to cover a concentration range from 0 $\mu g \cdot ml^{-1}$ to 10 $\mu g \cdot ml^{-1}$ of hexavalent chromium. Accurately pipette appropriate volumes of hexavalent chromium working standard solution (7.15.2) into individual, labelled, 100 ml one-mark volumetric flasks (8.2.2.2). Add 10 ml of soluble hexavalent extraction solution concentrate (7.12.1), if appropriate (see 11.2.1), dilute to the mark with water (7.1), stopper and mix thoroughly. Prepare these calibration solutions fresh daily.

11.3 Preparation of solutions for determination of insoluble hexavalent chromium compounds

11.3.1 Selection of sample preparation method for insoluble hexavalent chromium compounds

Use either the hotplate extraction method specified in 11.3.2 or the ultrasonic extraction method specified in 11.3.3 to prepare test solutions for determination of insoluble hexavalent chromium compounds.

NOTE 1 Spuriously high hexavalent chromium results can be obtained due to oxidation of soluble trivalent chromium compounds if these are present in the samples (see 13.4.3). This occurs more readily at higher temperatures, so ultrasonic extraction might be preferable to hotplate extraction if the samples could contain soluble trivalent chromium compounds. However, if the method specified in 11.2 is first used to prepare test solutions for determination of soluble hexavalent chromium compounds, soluble trivalent chromium compounds will also have been removed from the samples before extraction of insoluble hexavalent chromium takes place. If soluble trivalent chromium compounds could be present in the samples, consider adding magnesium hydroxide to protect against oxidation of trivalent chromium (see Reference [10]) or excluding air by purging with nitrogen (see Reference [21]).

NOTE 2 Useful background information on methods for determination of insoluble hexavalent chromium compounds in air and guidance on their use is given in Annex B. Further guidance can be found in a recently published critical review paper [19] on this topic.

11.3.2 Preparation of blank and sample test solutions for insoluble hexavalent chromium compounds using a hotplate

11.3.2.1 Open the filter transport cassettes, sampler filter cassettes or samplers (see 10.5) and transfer each filter into an individual labelled 50 ml beaker (8.2.2.1) using clean flat-tipped forceps (8.1.6.3). Alternatively, if the blank and sample filters were first extracted to produce test solutions for determination of soluble hexavalent chromium compounds, process together the extracted blank and sample filters and the secondary filters retained for analysis in 11.2.2.9.

11.3.2.2 Add 5 ml of insoluble hexavalent chromium extraction solution (7.12.3) to each beaker. If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the sampler form part of the sample (see Note 2 in 8.1.1), use the extraction solution to carefully wash any particulate material adhering to the internal surfaces of the sampler into the beaker.

11.3.2.3 Cover each beaker with a watch glass and swirl gently to mix the contents, ensuring that the filter remains completely immersed.

11.3.2.4 Place the beakers containing the filters and extraction solution on a hotplate (8.2.5) that is preheated to a surface temperature of 135 °C, and heat the solutions with occasional swirling for between 45 min and 60 min. Do not allow solutions to boil or evaporate to dryness. If necessary, the solutions should be kept topped up to 5 ml with water (7.1).

NOTE Evaporation to dryness can cause unwanted interconversion of hexavalent and trivalent chromium species. For example, air oxidation may cause oxidation of trivalent chromium to hexavalent chromium [10].

11.3.2.5 Remove the beakers from the hotplate and allow them to cool to room temperature.

11.3.2.6 Quantitatively transfer each blank and sample solution (11.3.2.5) to an individual, labelled, 10 ml volumetric flask (8.2.2.2), rinsing the watch glass, the insides of each beaker and the filter(s) and diluting to the mark with insoluble hexavalent chromium extraction solution (7.12.3). Stopper and mix thoroughly to produce the test solutions.

If necessary, remove any undissolved particulate or debris from disintegration of filters before transferring the solution to a volumetric flask and making to volume, e.g. by filtration or by centrifugation. Alternatively, filter test solutions prior to analysis using disposable syringe filters (see Note in 11.4.2.4).

11.3.3 Preparation of blank and sample test solutions for insoluble hexavalent chromium compounds using ultrasonic extraction

11.3.3.1 Open the filter transport cassettes, sampler filter cassettes or samplers (see 10.5) and transfer each filter into an individual, labelled tube (8.2.3.2) using clean flat-tipped forceps (8.1.6.3). Alternatively, if the blank and sample filters were first extracted to produce test solutions for determination of soluble hexavalent chromium compounds, process together the extracted blank and sample filters and the secondary filters retained for analysis in 11.2.2.9.

11.3.3.2 Add 5 ml of insoluble hexavalent chromium extraction solution (7.12.3) to each tube. If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the sampler form part of the sample (see Note 2 in 8.1.1), use the extraction solution to carefully wash any particulate material adhering to the internal surfaces of the sampler into the tube, utilising a filter funnel (8.2.3.3) to avoid spillage. Ensure that the filters are covered by the extraction solution. If necessary push them down with a clean glass or plastic rod until they are fully immersed. Then close each tube with its push-fit closure or screw cap.

Alternatively, the sample dissolution step specified in 11.3.3.2 may be carried out in the sampler if it is watertight when the sample air outlet orifice is sealed with its protective plug, if it is of sufficient capacity, and if the material of which it is constructed is resistant to the reagents used.

11.3.3.3 Adjust the water level in the ultrasonic bath (8.2.7) so that it is above the level of extraction solution in the tubes. Place the tubes in a suitable rack and load into the ultrasonic bath. Agitate the samples by applying ultrasound for 1 h [22].

11.3.3.4 After agitation, either

a) unscrew the caps or remove the push-fit closures from the tubes and dilute each blank and sample solution (11.3.3.3) to the 10 ml graduation of the tube with insoluble hexavalent chromium extraction solution (7.12.3). Reseal each tube with its screw cap or push-fit closure and mix thoroughly to produce the test solution,

or

b) quantitatively transfer each blank and sample solution (11.3.3.3) to an individual, labelled, 10 ml volumetric flask (8.2.2.2), rinsing out the tube and diluting to the mark with insoluble hexavalent chromium extraction solution (7.12.3). Stopper and mix thoroughly to produce the test solutions.

If necessary, remove any undissolved particulate or debris from disintegration of filters, e.g. by filtration or by centrifugation. Alternatively, filter test solutions prior to analysis using disposable syringe filters (see Note in 11.4.2.4).

11.3.4 Preparation of calibration solutions

Prepare a minimum of six calibration solutions, including a calibration blank solution, to cover a concentration range from 0 $\mu g \cdot ml^{-1}$ to 10 $\mu g \cdot ml^{-1}$ of hexavalent chromium. Accurately pipette appropriate volumes of hexavalent chromium working standard solution (7.15.2) into individual, labelled, 100 ml one-mark volumetric flasks (8.2.2.2). Dilute to the mark with insoluble hexavalent chromium extraction solution (7.12.3), stopper and mix thoroughly. Prepare these calibration solutions fresh daily.

11.4 Instrumental analysis

11.4.1 Setting up the instrument

11.4.1.1 Set up the ion chromatograph in accordance with manufacturer's instructions, as shown in Figure 2.

11.4.1.2 Install a sample loop that gives a suitable injection volume, e.g. 100 µl.

11.4.1.3 Adjust the visible detector to measure absorbance at 540 nm.

11.4.1.4 Adjust the flow rate of the eluent (7.13.2) to a value that is compatible with the columns used.

11.4.1.5 Adjust the flow rate of the diphenylcarbazide reagent solution (7.16) to a suitable value.

It is important that the ratio between the eluent and reagent flow rates be kept constant, that the total flow rate not exceed the maximum flow rate for the detector, and that the reagent be present in excess. A typical value for the ratio of the eluent flow rate to reagent flow rate is 3:1.

11.4.1.6 Measure the pH of the detector effluent using pH indicator paper (7.14) or a pH meter (8.2.9) and, if necessary, adjust the effluent pH to pH 2 or lower by decreasing the ratio of eluent flow rate to reagent flow rate or increasing the sulfuric acid concentration of the diphenylcarbazide reagent. After the flow rates are adjusted, allow the system to equilibrate for 15 min.

NOTE The pH needs to be low to ensure a quantitative reaction of 1,5-diphenylcarbazide with hexavalent chromium.

11.4.2 Analysis

11.4.2.1 If appropriate, the instrument shall be calibrated separately for analysis of soluble hexavalent chromium compounds and insoluble hexavalent chromium compounds, because of the need to matrix-match calibration and test solutions.

11.4.2.2 Inject the calibration solutions (11.2.3 or 11.3.4) into the ion chromatography system in order of increasing concentration and measure the absorbance of the hexavalent chromium peak for each calibration solution, either in peak height or peak area mode.

11.4.2.3 Use the instrument's computer to generate a calibration function using a linear regression. Repeat the calibration if the correlation coefficient, R^2, is not $\geqslant 0{,}999$.

NOTE 1 If $R^2 < 0{,}999$, it might be possible to remove an erroneous calibration point and reprocess the data to obtain an acceptable calibration.

NOTE 2 For instruments not equipped with a computer and data processing software that can prepare a calibration function, a calibration graph may be prepared manually by plotting the absorbance of the calibration solutions versus the concentration of hexavalent chromium, in micrograms per litre.

11.4.2.4 Inject the blank and sample test solutions (11.2.2.8, 11.3.2.6 or 11.3.3.4) into the ion chromatography system and make absorbance measurements for each solution. Use the stored calibration function (11.4.2.3) to determine the concentration of hexavalent chromium, in micrograms per litre.

For instruments not equipped with a computer and suitable data processing software (see Note 2 in 11.4.2.3), use the manually plotted calibration graph to determine the concentration of hexavalent chromium, in micrograms per litre.

NOTE It is a sensible precaution to filter all test solutions before injection in order to prevent possible plugging of the column or tubing. If the test solutions were not filtered or centrifuged during preparation (see 11.2.2.5, 11.3.2.6 and 11.3.3.4), consideration should be given to filtering them prior to analysis using disposable syringe filters.

11.4.2.5 Analyse the calibration blank solution and a mid-range calibration solution after the initial calibration, and again after every ten test solutions. If the measured concentration of hexavalent chromium in the continuing calibration blank is greater than three times the instrumental detection limit, as determined in 11.5.2, or if the measured concentration of hexavalent chromium in the continuing calibration verification has changed by more than ± 5 %, take one of the following corrective measures. Either use the instrument software to correct for the sensitivity change (reslope facility), or suspend analysis and recalibrate the instrument. In either case, reanalyse the test solutions that were analysed during the period in which the sensitivity change occurred, or if this is not possible, reprocess the data to take account of the sensitivity change.

11.4.2.6 Analyse reagent blank and laboratory blank solutions as specified in 11.6.1.1, and quality control solutions as specified in 11.6.2.1, and use the results to monitor the performance of the method as specified in 11.6.1.2 and 11.6.2.2.

11.4.2.7 If concentrations of hexavalent chromium are found to be above the upper limit of the linear calibration range, dilute the test solutions in order to bring them within the linear range and repeat the analysis. Add an appropriate volume of extraction solution (7.12.2 or 7.12.3) when making dilutions, so that the diluted test solutions and the calibration solutions are matrix-matched, and record the dilution factor.

NOTE For samples expected to have very high concentrations of hexavalent chromium, it might be necessary to dilute the test solutions before they are first analysed. Otherwise, swamping of the diphenylcarbazide reagent occurs and no colour develops.

11.4.2.8 Calculate the mean hexavalent chromium concentration of the blank test solutions.

11.5 Estimation of detection and quantification limits

11.5.1 Estimation of instrumental detection limit(s)

11.5.1.1 Estimate the instrumental detection limit(s) for determination of soluble hexavalent chromium and/or for determination of insoluble hexavalent chromium under the working analytical conditions following the procedure described in 11.5.1.2 and 11.5.1.3, and repeat this exercise whenever the experimental conditions are changed significantly.

NOTE The instrumental detection limit is of use in identifying changes in instrument performance, but it is not a method detection limit [23]. The instrumental detection limit is likely to be lower than the method detection limit because it only takes into account the variability between individual instrumental readings; determinations made on one solution do not take into consideration contributions to variability from the matrix or sample dissolution procedure.

11.5.1.2 Prepare a test solution with a hexavalent chromium concentration near the anticipated detection limit, e.g. 0,01 $\mu g \cdot l^{-1}$ of hexavalent chromium, by diluting the low hexavalent chromium calibration solution (11.2.3 or 11.3.4) by an appropriate factor with calibration blank solution (11.2.3 or 11.3.4).

11.5.1.3 Make at least ten ion chromatographic measurements on the test solution and calculate the instrumental detection limit as three times the sample standard deviation of the mean concentration value.

NOTE An alternative procedure for estimating the instrumental detection limit involves the analysis of calibration blank solution fortified with the hexavalent chromium at concentrations spanning the predicted detection limit [23].

11.5.2 Estimation of the method detection limit and quantification limit(s)

11.5.2.1 Estimate the method detection limit(s) and quantification limit(s) for determination of soluble hexavalent chromium and/or for determination of insoluble hexavalent chromium under the working analytical conditions following the procedure described in 11.5.2.2 and 11.5.2.3, and repeat this exercise whenever the experimental conditions are changed significantly.

11.5.2.2 Fortify at least ten filters (8.1.2) with hexavalent chromium near the anticipated detection limit, e.g. 0,01 µg of hexavalent chromium, by spiking the filter with 0,1 ml of a suitable calibration solution (11.2.3 or 11.3.4) and prepare test solutions from the filters following the sample dissolution procedure used to prepare the sample test solutions (see 11.2 or 11.3).

11.5.2.3 Make ion chromatographic measurements on the test solutions (11.5.2.2) and calculate the method detection limit and the quantification limit as three times and ten times the sample standard deviation of the mean concentration, respectively.

11.6 Quality control

11.6.1 Reagent blanks and laboratory filter blanks

11.6.1.1 Carry reagent blanks (see 3.4.7) and laboratory blanks (see 3.4.5) through the entire sample preparation and analytical process to determine whether the samples are being contaminated from laboratory activities. Prepare reagent blank solutions and laboratory blank solutions according to a frequency of at least 1 per 20 samples or a minimum of one per batch.

11.6.1.2 If results for reagent blanks and/or laboratory blanks are significantly higher than expected, based on previous experience, investigate whether contamination is occurring from laboratory activities and/or the batch of filters used for sampling and take appropriate corrective action to ensure that this does not re-occur.

11.6.2 Quality control solutions

11.6.2.1 Carry spiked samples and spiked duplicate samples throughout the entire sample preparation and analytical process to estimate the method accuracy on the sample batch, expressed as a percent recovery relative to the true spiked value. Spiked samples consist of filters to which known amounts of hexavalent chromium have been added. (This can be accomplished by spiking with known volumes of working hexavalent chromium standard solution at amounts within the linear dynamic range of the instrument. The working hexavalent chromium standard solution used shall be prepared from a stock standard hexavalent chromium solution from a different source than that used for preparing the calibration solutions.) Prepare and analyse these quality control solutions according to a frequency of at least 1 per 20 samples or a minimum of one per batch.

11.6.2.2 Monitor the performance of the method by plotting control charts of the relative percent recoveries and of the relative percent differences between the spiked samples. If quality control results indicate that the method is out of control, investigate the reasons for this, take corrective action and reanalyse the samples if necessary. See ASTM 882-87 [24] for general guidance on the use of quality control charts.

11.6.3 Certified reference materials (CRMs)

If available, CRMs for hexavalent chromium shall be analysed prior to routine use of the method to establish that the percent recovery relative to the certified value is satisfactory.

11.6.4 External quality assessment

If laboratories carry out hexavalent chromium in air analysis on a regular basis, it is recommended that they participate in a relevant external quality assessment scheme or proficiency testing scheme, if such a scheme exists and they have access to it.

11.7 Measurement uncertainty

It is strongly recommended that laboratories estimate and report the uncertainty of their measurements in accordance with the GUM[7]. The first step is to construct a cause-and-effect diagram[25] to identify the individual sources of random and systematic error in the method. These are then estimated and/or determined experimentally and combined in an uncertainty budget. Finally, the combined uncertainty is multiplied by an appropriate coverage factor to produce an expanded uncertainty. A coverage factor of 2 is recommended, which gives a level of confidence of approximately 95 % in the calculated value.

NOTE 1 References [26] and [27] describe the application of cause-and-effect analysis to analytical methods.

NOTE 2 Terms that contribute to the random variability of the method are generally accounted for in the measurement precision, which can be determined from quality control data. Error associated with instrumental drift can be estimated, assuming a rectangular probability distribution, by dividing the drift permitted before the instrument is recalibrated by $\sqrt{3}$ (see 11.4.2.5).

NOTE 3 Systematic errors include, for example, those associated with method recovery, sample recovery, preparation of working standard solutions, dilution of test solutions, etc.

12 Expression of results

Calculate the mass concentration of hexavalent chromium in the air samples at ambient conditions, using the equation:

$$\rho_{\mathrm{Cr(VI)}} = \frac{\left(\rho_{\mathrm{Cr(VI)},1} \times V_1 \times F\right) - \left(\rho_{\mathrm{Cr(VI)},0} \times V_0\right)}{V} \qquad (2)$$

where

$\rho_{\mathrm{Cr(VI)}}$ the calculated mass concentration of hexavalent chromium in the air sample, in micrograms per cubic metre,

$\rho_{\mathrm{Cr(VI)},0}$ is the mean mass concentration of hexavalent chromium in the field blank test solutions, in micrograms per litre;

$\rho_{\mathrm{Cr(VI)},1}$ is the mass concentration of hexavalent chromium in the sample test solution, in micrograms per litre;

V is the volume, in litres, of the air sample;

V_0 is the volume, in millilitres, of the field blank test solution;

V_1 is the volume, in millilitres, of the sample test solution; and

F is the dilution factor ($F = 1$ in the absence of dilution).

13 Method performance

13.1 Sample collection and stability

Laboratory testing with generated atmospheres of chromic acid mist yielded a collection efficiency of 94,5 % over the range 0,5 $\mu g \cdot m^{-3}$ to 10 $\mu g \cdot m^{-3}$ of hexavalent chromium on polyvinyl chloride (PVC) filters of pore size 5 µm [28]; 96,0 % recovery of hexavalent chromium was found two weeks after sample collection[29]. PVC filter samples generated from chromate-containing paint aerosols demonstrated no change in hexavalent chromium recoveries after two weeks[30]. Long-term sample stability has also been demonstrated for hexavalent chromium in welding fume collected on binder-free quartz fibre filters [31]. However, cellulose filters and at least one type of PVC filter have been shown to cause reduction of hexavalent chromium over time[32][33]. Rapid reduction of hexavalent chromium has also been observed in certain work environments, e.g. plating works[34], and filters may be treated with alkali in order to minimise this reduction[11].

13.2 Hotplate extraction

Quantitative recoveries have been obtained for both soluble and insoluble chromates using sodium carbonate/sodium hydrogen carbonate and sodium carbonate/sodium hydroxide extraction solutions[10][35]. Negligible biases were found, and overall accuracies were ± 12,9 % for the former extraction solution[10] and ± 16,5 % for the latter [35]. Method detection limits for the former and latter extraction solutions were found to be 0,01 µg and 0,02 µg of hexavalent chromium per filter, respectively. Recoveries of hexavalent chromium from a certified reference material generated from welding dust were quantitative for both extraction solutions [35][36].

13.3 Ultrasonic extraction

Quantitative recoveries have been obtained for both soluble and insoluble chromates using sodium hydroxide/sodium carbonate extraction solution[22][37]. Negligible biases were found, and overall accuracy was ± 16,8 %. When using a solid-phase extraction procedure to isolate hexavalent chromium, the method detection limit was found to be 0,09 µg of hexavalent chromium per filter [22]. The method detection limit for determination of hexavalent chromium by ion chromatography is probably lower, but has not yet been evaluated. Quantitative recoveries of hexavalent chromium were obtained from a certified reference material generated from welding dust [22][35].

13.4 Interferences

13.4.1 Hexavalent chromium can be reduced to trivalent chromium by reaction with certain filter materials. Advice on appropriate filter selection is given to ensure that this problem does not occur (see 8.1.2).

13.4.2 Hexavalent chromium can be reduced to trivalent chromium by reaction with other substances present in the test atmosphere. In particular, reduction of hexavalent chromium can occur on the filter, prior to extraction, by reaction with dust that contains oxidizable material, such as metal from grinding operations, organic particulate matter, etc. This is a particular problem when measuring hexavalent chromium in chromic acid mists [34], but its effect can be alleviated to a certain extent by impregnating the filter with alkali (see Note in 8.1.2). Hexavalent chromium can also be reduced to trivalent chromium during extraction from the sample due to reaction with reducing agents such as divalent iron, which, for example, co-exists with hexavalent chromium in many welding fumes. This problem is minimized in the described procedure by use of alkaline extraction solutions.

13.4.3 Trivalent chromium can be oxidized to hexavalent chromium in hot alkaline solutions. Therefore, if soluble trivalent chromium compounds are likely to be present in the test atmosphere it is recommended that the ultrasonic method be used for extraction of insoluble hexavalent chromium compounds, since this is carried out at a lower temperature than the hotplate method. Alternative possibilities are to add magnesium hydroxide to protect against air oxidation of trivalent chromium[10] or exclude air by purging with nitrogen[21]. Both of these approaches are mentioned in this International Standard, but they are not included in the normative procedure. Trivalent chromium can also be oxidized to hexavalent chromium during hot alkaline extraction, due to reaction with oxidizing agents such as manganese dioxide[38], which, for example, co-exists with soluble trivalent chromium in certain welding fumes. Once again, this problem can be alleviated by use of the lower temperature ultrasonic extraction method and/or by the addition of magnesium hydroxide.

NOTE See Annex B for further guidance on methods for determination of hexavalent chromium in air.

14 Special cases

14.1 Spray-painting

Evidence indicates that in some cases the use of a more alkaline extraction solution is necessary to recover hexavalent chromium from samples collected during spray-painting operations [39]. This is due to the resistant properties of the paints concerned. An alternative extraction procedure with 50 $g \cdot l^{-1}$ sodium hydroxide and 75 $g \cdot l^{-1}$ sodium carbonate solution, suitable for use in such circumstances, is described elsewhere [10].

14.2 Action to be taken when particles have become dislodged from the filter during transportation

When the filter transport cassettes or samplers are opened, it is advisable to look for evidence that particles have become dislodged from the filter during transportation. If this appears to have occurred, consider whether to discard the sample as invalid, or whether to wash the internal surfaces of the filter transport cassette or sampler into the sample dissolution vessel in order to recover the material concerned.

15 Test report

15.1 Test record

A comprehensive record of the test performed shall be maintained, including the following information:

a) a statement to indicate the confidentiality of the information supplied, if appropriate;

b) a complete identification of the air sample, including the date of sampling, the place of sampling, the type of sample (personal or static), either the identity of the individual whose breathing zone was sampled (or other personal identifier) or the location at which the general occupational environment was sampled (for a static sample), a very brief description of the work activities that were carried out during the sampling period, and a unique sample identification code;

c) a reference to this International Standard;

d) the make, type and diameter of filter used;

e) the make and type of sampler used;

f) the make and type of sampling pump used, and its identification;

g) the make and type of flowmeter used, the primary standard against which the calibration of the flowmeter was checked, the range of flow rates over which the calibration of the flowmeter was checked, and the atmospheric temperature and pressure at which the calibration of the flowmeter was checked, if appropriate (see 10.1.3);

h) the time at the start and at the end of the sampling period, and the duration of the sampling period, in minutes;

i) the mean flow rate during the sampling period, in litres per minute;

j) the mean atmospheric temperature and pressure during the sampling period, if appropriate (see 10.1.3);

k) the volume of air sampled, in litres, at ambient conditions;

l) the name of the person who collected the sample;

m) the time-weighted average mass concentration of hexavalent chromium found in the air sample (in $\mu g \cdot m^{-3}$), at ambient temperature and pressure, or, if appropriate, adjusted to reference conditions;

n) details of the sample extraction method(s) used;

o) the analytical variables used to calculate the result, including the concentrations of hexavalent chromium in the blank and sample test solutions, the volumes of the blank and sample test solutions, and the dilution factor, if applicable;

NOTE If necessary data (e.g. the volume of air sampled) are not available to the laboratory for the above calculations to be carried out, the laboratory report may contain the analytical result in nanograms of hexavalent chromium per filter sample.

p) the type(s) of instrument(s) used for sample preparation and analysis, and unique identifiers(s);

q) the estimated instrumental detection limits, method detection limits and quantification limits under the working analytical conditions; the measurement uncertainty determined in accordance with the GUM [7]; and, if requested by the customer, quality control data;

r) any operation not specified in this International Standard, or regarded as optional;

s) the name of the analyst(s) [or other unique identifier(s)];

t) the date of the analysis; and

u) any inadvertent deviations, unusual occurrences, or other notable observations.

15.2 Laboratory report

The laboratory report shall contain all information required by the end user, regulatory authorities and accreditation organizations.

Annex A
(informative)

Temperature and pressure corrections

A.1 Temperature and pressure corrections for the indicated volumetric flow rate

A.1.1 Bubble flowmeters are preferred for measuring the volumetric flow rate because the readings they give are independent of temperature and pressure. For other flowmeters, it might be necessary to apply a correction to the indicated volumetric flow rate if the temperature and pressure at the time of measurement is different to when the calibration of the flowmeter was checked.

A.1.2 A typical example of the need for a temperature and pressure correction is when a constant pressure drop, variable area, flowmeter is used to measure the volumetric flow rate. In this instance, use the following equation to calculate a corrected air sample volume:

$$V_{\mathrm{corr}} = q_V \times t \times \sqrt{\frac{p_1 \times T_2}{p_2 \times T_1}} \tag{A.1}$$

where:

V_{corr}	is the corrected volume, in litres;
q_V	is the mean flow rate, in litres per minute;
t	is the sampling time, in minutes;
p_1	is the atmospheric pressure, in kilopascals, during calibration of the sampling pump flowmeter;
p_2	is the mean atmospheric pressure, in kilopascals, during the sampling period;
T_1	is the temperature, in kelvins, during calibration of the sampling pump flowmeter; and
T_2	is the mean temperature, in kelvins, during the sampling period.

A.1.3 Any other flowmeter can also require a correction for variation in pressure and temperature. Follow the manufacturer's instructions for such corrections.

A.2 Recalculation of hexavalent chromium in air concentrations to reference conditions

If necessary (see 10.1.3.2), recalculate hexavalent chromium in air concentrations to reference conditions (e.g. 293 K and 101,3 kPa) using the following equation:

$$\rho_{\mathrm{Cr(VI),corr}} = \rho_{\mathrm{Cr(VI)}} \times \frac{(101{,}3 \times T_2)}{(p_2 \times 293)} \tag{A.2}$$

where

$\rho_{\mathrm{Cr(VI),corr}}$	is the corrected mass concentration of hexavalent chromium in the air sample, in milligrams per cubic metre, at reference conditions;
$\rho_{\mathrm{Cr(VI)}}$	is the mass concentration of hexavalent chromium in the air sample, in milligrams per cubic metre, at ambient conditions;
T_2	is the mean temperature, in kelvins, during the sampling period;
p_2	is the mean atmospheric pressure, in kilopascals, during the sampling period;
293	is the reference temperature, in kelvins; and
101,3	is the reference atmospheric pressure, in kilopascals.

Annex B
(informative)

Background on methods for determination of hexavalent chromium in air and guidance on their use

B.1 Background

B.1.1 A method that has been widely used for determination of hexavalent chromium is extraction with dilute sulfuric acid and spectrophotometric analysis of the magenta chromagen (λ_{max} = 540 nm) formed by reaction with 1,5-diphenylcarbazide[11][21][29]. This technique is satisfactory if there are no interferences from substances that can react with hexavalent chromium and change its valency state. However, for many applications, for example the determination of hexavalent chromium in welding fume, it is not applicable, since there is a high probability that redox reactions will lead to loss of hexavalent chromium during analysis. This latter problem is exacerbated by the low pH required for the diphenylcarbazide reaction itself, as hexavalent chromium is highly oxidizing under acidic conditions.

The presence of magnetite (Fe_3O_4) in many welding fumes means that if hexavalent chromium is extracted with dilute sulfuric acid, it is almost completely reduced before measurement. Thomsen and Stern [40] developed a scheme for separate determination of soluble and insoluble hexavalent chromium compounds intended to overcome this problem. They used water to extract soluble hexavalent chromium compounds, followed by a hotplate extraction with 70 g·l^{-1} sodium carbonate solution to extract insoluble chromates. The mechanism for dissolution of insoluble chromates using this method is described by the following equation:

$$MCrO_4 + CO_3^{2-} \rightleftharpoons MCO_3 + CrO_4^{2-} \qquad (B.1)$$

In the presence of a large excess of carbonate, the equilibrium is shifted quantitatively to the right and insoluble chromates are taken into solution. Equally important, however, the principal reducing component of welding fume, divalent iron, has a low solubility in the alkaline extraction solution, so the potential for loss of hexavalent chromium is greatly reduced. Conveniently, the solubility of many other metal species, including trivalent chromium, trivalent iron and divalent nickel, is also low at high pH, and, furthermore, hexavalent chromium is less oxidizing under alkaline conditions.

The effect of pH on the distribution of chromium between trivalent and hexavalent oxidation states in the presence of iron is described by the following equation:

$$Cr(OH)_3 + 5\ OH^- + 3\ Fe^{3+} \rightleftharpoons CrO_4^{\ 2-} + 4\ H_2O + 3\ Fe^{2+} \qquad (B.2)$$

It follows that a decrease in pH is accompanied by a reduction of hexavalent chromium, whereas higher pHs lead to oxidation of trivalent chromium. Thomsen and Stern[40] considered this and concluded that the ideal pH for extraction of hexavalent chromium should be around pH 8. However, they found that an increase in the alkalinity did not produce oxidation of trivalent chromium, and this observation was attributed to a low reaction rate at the temperature used in the analysis (< 100 °C).

OSHA[41] subsequently modified the procedure described by Thomsen and Stern[40], using 100 g·l^{-1} sodium carbonate/20 g·l^{-1} sodium hydrogen carbonate solution, rather than 70 g·l^{-1} sodium carbonate solution, to extract hexavalent chromium. This was thought to offer greater stability and improved extraction efficiency for the more insoluble chromates.

B.1.2 Blakely and Zatka[42] also developed a procedure for separate determination of soluble and insoluble hexavalent chromium compounds. They used 10 g·l^{-1} sodium carbonate solution to extract 'soluble' hexavalent chromium and hotplate extraction with 20 g·l^{-1} sodium hydroxide/30 g·l^{-1} sodium carbonate solution for insoluble chromates. Subsequently, Zatka reported[43] that air oxidation of trivalent chromium could occur using hot alkaline extraction and recommended the addition of magnesium hydroxide to prevent it. Zatka's theory on the effect of magnesium hydroxide is given below.

The chemical behaviour of trivalent chromium in alkaline solution is expressed by:

$$Cr^{3+} + 3\ OH^- \rightleftharpoons Cr(OH)_3 \text{ and } Cr(OH)_3 + OH^- \rightleftharpoons [Cr(OH)_4]^- \qquad (B.3)$$

The hydroxo complex, $[Cr(OH)_4]^-$, is heat-sensitive, and near the boiling point tends to decompose irreversibly:

$$[Cr(OH)_4]^- \rightarrow CrO(OH) + H_2O + OH^- \qquad (B.4)$$

In accordance with this equation, increase of alkalinity will decrease decomposition of the complex.

Zatka's experiments lead to the conclusion that the only species that can undergo air oxidation is the hydroxocomplex:

$$4\ [Cr(OH)_4]^- + 3\ O_2 + 4\ OH^- \rightarrow 4\ CrO_4{}^{2-} + 10\ H_2O \qquad (B.5)$$

During sample digestion, the hydroxocomplex is involved in both reactions, decomposition [Equation (B.4)] and oxidation [Equation (B.5)]. Decomposition is most favourable, but when the alkalinity of the solution is increased, decomposition of the hydroxocomplex is suppressed and more hexavalent chromium can be formed. This can be counteracted by the addition of magnesium hydroxide, which forms a precipitate that adsorbs the hydrous chromium(**III**) oxide, CrO(OH). This shifts Equation (B.4) to the right and greatly reduces the extent to which trivalent chromium undergoes air oxidation. It should also be noted that the hydroxocomplex is decomposed more readily at higher temperatures, so extraction at lower temperatures is favoured.

Zatka's recommendation[43] that magnesium hydroxide should be used to prevent air oxidation of trivalent chromium was subsequently taken up by OSHA[10], whilst NIOSH[21] opted to eliminate air oxidation by degassing the extraction solution with nitrogen and purging the headspace above it with nitrogen throughout the extraction procedure. However, it is not usually necessary to take measures to prevent air oxidation. The effect of air oxidation is only of importance if there is a significant concentration of trivalent chromium in the sample solution, if the hexavalent chromium-in-air concentration is low and yet still of significance in relation to the limit value, and if the extraction conditions are favourable (i.e. high temperature and alkalinity).

B.1.3 In addition to air oxidation, trivalent chromium can theoretically be oxidized to hexavalent chromium by redox reaction with other substances found in workplace air, such as manganese dioxide[38], which is present in many welding fumes. Like air oxidation, if chemical oxidation does occur, it will do so to a greater extent at higher temperatures, and it can also be protected against by the addition of magnesium hydroxide.

B.1.4 Other extraction solutions have been used for hexavalent chromium. In particular, Karwas[44] used an ammonium sulfate/ammonium hydroxide extraction solution, claiming that it decreases oxidation of trivalent chromium by between 65 % and 95 % due to the formation of a kinetically stable hexa-coordinated complex $[Cr(NH_3)_6]^{3+}$. Use of an ammonium sulfate/ammonium hydroxide extraction solution has also been described by NIOSH[45]. However, Goodman et al.[46] found that this solution is not alkaline enough for effective extraction of hexavalent chromium from insoluble compounds such as lead chromate and barium chromate.

B.1.5 There is increasing interest in separate determination of soluble hexavalent chromium compounds and insoluble hexavalent chromium compounds, and it was therefore decided to include an extraction method for soluble hexavalent chromium compounds in this International Standard. Water[42], 0,5 N sulfuric acid [11][30] and 10 $g \cdot l^{-1}$ sodium carbonate solution [43] have been used to extract soluble hexavalent chromium compounds, but none of these extraction solutions is entirely satisfactory. Extraction with 0,5 N sulfuric acid gives low soluble hexavalent chromium results if the samples contain substances that can reduce hexavalent chromium, e.g. divalent iron. This could also be a problem for extraction with water. Furthermore, extraction with water has been found to give low soluble hexavalent chromium results in the presence of soluble trivalent chromium compounds. Extraction with 10 $g \cdot l^{-1}$ sodium carbonate solution overcomes both of these problems. However, the method does not strictly determine water-soluble hexavalent chromium and, where they have been set, national exposure limits generally relate to this.

B.2 Guidance on the use of methods for determination of hexavalent chromium in air

B.2.1 Sampling considerations

Reduction of hexavalent chromium can occur by reaction with many of the polymeric materials from which filters used for air sampling are manufactured. Careful selection of the filter used for collecting hexavalent chromium is therefore of paramount importance (see 8.1.2).

Hexavalent chromium can also be reduced to trivalent chromium on the sample filter by reaction with other substances found in workplace air, e.g. hexavalent chromium can react with dust containing oxidizable material such as metal from grinding operations, organic particulate matter, etc. This can be a particular problem when measuring hexavalent chromium in chromic acid mists [34], because hexavalent chromium is easily reduced in an acidic environment. Impregnation of the filter with alkali is recommended in such circumstances (see Note in 8.1.2), but it is not a perfect solution to what is probably an intractable problem.

B.2.2 Determination of soluble hexavalent chromium

The method prescribed for determination of soluble hexavalent chromium compounds permits the use of either water or ammonium sulfate/ammonium hydroxide solution for extraction. However, the following points should be considered when deciding which to use.

- The two methods do not necessarily give equivalent results.
- Extraction with water could give low soluble hexavalent chromium results if the samples also contain soluble trivalent chromium compounds (see B.1.5). Therefore, use of ammonium sulfate/ammonium hydroxide solution is recommended for extraction when both could be present in the test atmosphere, e.g. in chromium plating works where both trivalent and hexavalent chromium plating solutions are in use.
- Extraction with water could also give low soluble hexavalent chromium results if the samples contain substances that can reduce hexavalent chromium, e.g. divalent iron (see B.1.1). Therefore, use of ammonium sulfate/ammonium hydroxide solution is recommended for extraction when analysing such samples, e.g. welding fume.

If it is believed that only soluble hexavalent chromium compounds are present in the test atmosphere and there is a concern that the method could give low soluble hexavalent chromium results, an alternative approach is to determine total hexavalent chromium and assume that all the hexavalent chromium is in the soluble form.

B.2.3 Determination of insoluble hexavalent chromium

The method prescribed for determination of insoluble hexavalent chromium compounds permits the use of either hotplate or ultrasonic extraction using 20 $g \cdot l^{-1}$ sodium hydroxide/30 $g \cdot l^{-1}$ sodium carbonate solution. However, the following points should be considered when deciding which to use.

- If soluble trivalent chromium compounds are present in the sample, they can be oxidized to hexavalent chromium during hotplate extraction of insoluble hexavalent chromium compounds, giving spuriously high results (see B.1.2 and B.1.3). Therefore, if soluble trivalent chromium compounds could be present in the test atmosphere, it is preferable to use ultrasonic extraction rather than hotplate extraction, as oxidation of trivalent chromium is less likely to occur at the lower extraction temperature involved.
- If measurements are required only for comparison with a limit value for insoluble or total hexavalent chromium compounds, soluble hexavalent chromium would not normally be separately determined. However, if soluble trivalent chromium compounds could be present in the test atmosphere, it might be beneficial to apply the soluble hexavalent chromium extraction method prior to extraction of insoluble hexavalent chromium compounds, even if there is no national exposure limit for soluble hexavalent chromium compounds. In this way, soluble trivalent chromium compounds could be removed from the sample before the insoluble hexavalent chromium extraction method is applied, which might avoid the possibility that they could be oxidized to hexavalent chromium during extraction of insoluble hexavalent chromium.

- Alternatively, magnesium hydroxide could be added to protect against air oxidation of soluble trivalent chromium, as described by OSHA[10], or oxygen could be excluded by degassing the extraction solution and purging the headspace above it with nitrogen throughout the extraction procedure, as described by NIOSH[21]. However, anecdotal evidence exists that use of magnesium hydroxide can lead to some loss of hexavalent chromium due to co-precipitation.

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