Critical Review

Sampling and analysis considerations for the determination of hexavalent chromium in workplace air†

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Airborne hexavalent chromium (Cr[VI]) is a known human respiratory carcinogen and allergen. Workers in a variety of industries may be exposed to airborne hexavalent chromium, with exposures frequently occurring *via* inhalation and/or dermal contact. Analytical methods for the measurement of Cr(VI) compounds in workplace samples, rather than for the determination of total elemental chromium in workplace air, are often desired because exposure limit values for Cr(VI) compounds are much lower than for total Cr. For years, sampling and analytical test methods for airborne Cr(VI) have been investigated so as to provide means for occupational exposure assessment to this highly toxic species. Inter-conversion of trivalent chromium (Cr[III]) and Cr(VI) can sometimes occur during sampling and sample preparation, and efforts to minimize unwanted redox reactions involving these chromium valences have been sought. Because of differences in toxicity, there is also interest in the ability to differentiate between water-soluble and insoluble forms of Cr(VI), and procedures that provide solubility information concerning Cr(VI) compounds have been developed. This paper reviews the state of the art concerning the measurement of airborne Cr(VI) compounds in workplace aerosols and related samples.

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Left to right: Kevin Ashley, Alan Howe, Martine Demange and Olle Nygren

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1. Introduction

The health of workers in many industries is at risk through exposure to hexavalent chromium (Cr[vi]) compounds. Airborne Cr(vi) has been identified as a known human respiratory carcinogen,[1–6] and analytical methods for the measurement of this species in workplace aerosols are desired. Aside from carcinogenic effects, some Cr(vi) compounds have also been found to act as contact allergens.[7–10] Hexavalent chromium exposures in the workplace have been associated with numerous industries, including metal plating, chemical production, tanning, chromite ore processing, welding, and spray painting operations.[11–14] There is a strong desire on the part of the occupational and environmental health community to have the capability to accurately measure airborne Cr(vi) species at trace levels. Hence, in recent years the development of improved analytical methods for the determination of Cr(vi) in workplace air and other matrices has been a subject of significant interest.

Chromium in chemical compounds can assume oxidation states [−4] and [−2 to +6],[15] with states [0], [+2], [+3] and [+6] being those most commonly found in industry.[16,17] But in nature, chromium exists almost exclusively in two oxidation states, trivalent (Cr[iii]) and hexavalent. Chromium in the trivalent state is relatively non-toxic and is an essential nutrient in the human diet for the maintenance of effective glucose, lipid, and protein metabolism.[18] In contrast, the hexavalent species is highly toxic due to its ability to oxidize biomolecules, notably DNA.[19,20] Almost all Cr(vi) present in the environment comes from anthropogenic sources, as this species is ordinarily converted to Cr(iii) *via* natural and often rapid chemical reduction.[21–23] In occupational settings, airborne Cr(vi) compounds can be found in a wide range of concentrations and particle sizes, and also in the presence of Cr(iii) compounds with widely varying ratios.[24]

The toxicity of airborne Cr(vi) compounds is quite varied and depends in part on the solubility of the Cr(vi) compound in question.[25] Based on toxicity data, the American Conference of Governmental Industrial Hygienists (ACGIH) has promulgated various Threshold Limit Values® (TLVs) for a number of different chromium species that may be encountered in workplaces (Table 1).[26] It can be seen from Table 1 that the chromium concentration of interest (in terms of TLVs) can range from as low as 0.5 μg m^{-3} for strontium chromate

Table 1 ACGIH Threshold Limit Values® (TLVs) for chromium compounds.[26]

Substance(s)	TLV (TWA[a])	Comments
Calcium chromate, as Cr	0.001 mg m^{-3}	Suspected carcinogen
Chromite ore processing (chromate), as Cr	0.05 mg m^{-3}	Confirmed carcinogenicity
Chromium, and inorganic compounds, as Cr:		
Cr metal & Cr(III) compounds	0.5 mg m^{-3}	Allergens; no known carcinogenicity
Water–sol. Cr(VI) compounds	0.05 mg m^{-3}	Confirmed carcinogens
Insoluble Cr(VI) compounds	0.01 mg m^{-3}	Confirmed carcinogens; allergens
Lead chromate, as Cr	0.012 mg m^{-3}	Suspected carcinogen
Strontium chromate, as Cr	0.0005 mg m^{-3}	Suspected carcinogen
Zinc chromate, as Cr	0.01 mg m^{-3}	Confirmed carcinogen

[a](8-hour time-weighted average.)

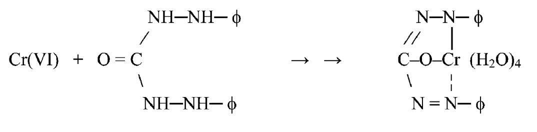
to as high as 0.5 mg m^{-3} for chromium metal (Cr[0]) and trivalent chromium compounds. This three order-of-magnitude range in TLVs presents significant analytical challenges, especially at lower chromium concentrations where it may be very difficult to attain sufficiently low detection limits. The analytical situation is further complicated by the potential desire to distinguish between soluble and insoluble forms of Cr(VI).

It is also necessary to consider additional analytical challenges which can be encountered owing to redox processes involving hexavalent and trivalent chromium compounds. In many cases, Cr(VI) can be reduced to Cr(III) during sampling and sample preparation, and under certain conditions Cr(III) can be oxidized to Cr(VI) during sample preparation processes. These redox reactions depend greatly on factors such as (a) the ratio of Cr(VI) species to Cr(III) species in the sample, and (b) the presence or absence of other compounds (*e.g.*, Fe(II), organics, peroxides) in the matrix that could facilitate oxidation of Cr(III) and/or reduction of Cr(VI). Also, solution pH has a major influence on the relative thermodynamic stability of Cr(III) and Cr(VI) species. These and other issues must be taken into account during sampling and analytical method development and evaluation for the determination of Cr(VI) species in workplace air environments.

2. Background

2.1 Cr(VI) reaction with 1,5-diphenylcarbazide

A method that has been widely used for the determination of airborne Cr(VI) in the workplace entails extraction of air filter samples with sulfuric or nitric acid.[27–29] Extraction is followed by spectrophotometric analysis of the magenta chromagen ($\lambda_{max} = 540$ nm) which is formed by the reaction of Cr(VI) with 1,5-diphenylcarbazide (DPC) in strongly acidic solution:[30–32]



1,5-diphenylcarbazide **Cr-diphenylcarbazone complex**

The result of the reaction sequence is the formation of the highly colored carbazone inner complex salt of a chromous ion (Cr[II]).[33] This complex can be measured spectrophotometrically at 540 nm with extremely high detection power; for example, method detection limits as low as ~0.1 ng Cr(VI) per air filter sample have been attained.[34] Although the chemistry described above has been known for over a century, the overall reaction mechanism is still not fully understood. The reaction is highly specific for Cr(VI) (*vs.* Cr[III]), although several other metal species are also known to react with DPC, *i.e.*, Cu(II), Fe(III), Hg(II), Mo(VI), and V(V).[35]

The acid extraction–DPC spectrophotometric technique is satisfactory if there are no interferences from substances which can: (a) react with Cr(VI) and change its valence state; and/or (b) react with DPC and thereby compete with Cr(VI) for the colorimetric reagent. For many applications, *e.g.*, the determination of Cr(VI) in welding fumes, the direct DPC procedure is not applicable, since there is a high probability that redox reactions will lead to the loss of Cr(VI) during analysis. This latter problem is exacerbated by the low pH required for the Cr(VI)–DPC reaction itself, as Cr(VI) is easily reduced under acidic conditions. For instance, the presence of magnetite (Fe_3O_4) in many welding fumes means that if Cr(VI) is extracted with dilute acid, it will be almost completely reduced to Cr(III) by Fe(II) before DPC measurement. Other air sample matrices having significant concentrations of Fe(II) species will be prone to the same problem, for instance, aerosols generated from concrete substrates that contain chromates and iron compounds. Moreover, high concentrations of other metal interferants (*e.g.*, those mentioned in the preceding paragraph) could swamp the desired chromate reaction with DPC.

2.2 Influence of pH

Cr(VI) compounds, especially soluble forms, can be reduced to Cr(III) species when chromates in airborne particulate matter are captured on filter media.[36–39] Such is particularly true under acidic conditions. This is because in acid media, the standard reduction potential for the Cr(VI)/Cr(III) redox couple is positive, thereby favoring stabilization of Cr(III):[40]

$$\mathrm{HCrO_4^-} + 7\mathrm{H^+} + 3\mathrm{e^-} \leftrightarrow \mathrm{Cr^{3+}} + 4\mathrm{H_2O};$$
$$E^\circ = +1.21\ \mathrm{V}\ (\mathrm{pH}\ 1)$$

In alkaline media, however, the redox equilibrium is shifted considerably and favors the stabilization of Cr(VI):[41]

$$\mathrm{CrO_4^{2-}} + 4\mathrm{H_2O} + 3\mathrm{e^-} \leftrightarrow \mathrm{Cr(OH)_2^+} + 6\mathrm{OH^-};$$
$$E^\circ = -0.13\ \mathrm{V}\ (\mathrm{pH}\ 14)$$

Below pH 10, Cr(VI) predominates as anionic species (CrO_4^{2-}, $HCrO_4^-$), whereas Cr(III) exists as cations (Cr^{3+}, $Cr(OH)^{2+}$, $Cr(OH)_2^+$).[42] Protonation/deprotonation of Cr(III) is kinetically rapid,[41] further emphasizing the importance of solution acidity or basicity. Hence pH is an extremely important factor for consideration of the relative stabilities of Cr(III) and Cr(VI) species in aqueous solutions.

In an attempt to overcome the problem of Cr(VI) reduction by Fe(II) when analyzing welding fume samples, an extraction scheme was developed for the separate determination of soluble and insoluble Cr(VI) compounds.[43] First water was used to extract soluble Cr(VI) compounds, and this was followed by hotplate extraction with a sodium carbonate solution to extract insoluble chromates. The dissolution of insoluble Cr(VI) compounds is described by:

$$\mathrm{MCrO_4} + \mathrm{CO_3^{2-}} \leftrightarrow \mathrm{MCO_3} + \mathrm{CrO_4^{2-}}$$

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 is the fact that the principal reducing component of welding fume, *i.e.*, divalent iron, has low solubility in the alkaline extraction solution, so the potential for loss of Cr(VI) is greatly reduced. Conveniently, the solubilities of many other metal species, including Fe(III) and Cr(III), are also low at high pH. Moreover, Cr(VI) is less easily reduced under alkaline conditions.

The effect of pH on the distribution of chromium oxidation states (between trivalent and hexavalent) in the presence of ferric and/or ferrous ions is described by the following equilibrium:

$$Cr(OH)_3 + 5OH^- + 3Fe^{3+} \leftrightarrow CrO_4^{2-} + 4H_2O + 3Fe^{2+}$$

It follows that a decrease in pH is accompanied by the reduction of Cr(VI), whereas high pH conditions lead to the oxidation of Cr(III). These considerations led to a conclusion that the ideal pH for extraction of Cr(VI) should be around pH 8.[43] Fortuitously, it was also found that an increase in alkalinity did not produce significant oxidation of Cr(III). This observation was attributed to a low reaction rate at the temperature used during extraction (<100 °C). The above alkaline dissolution procedure was subsequently modified in the promulgation of an official method in the USA for the determination of Cr(VI) in workplace air samples.[44] The modified method, which used a stronger carbonate buffer for extraction, was thought to offer greater stability and improved extraction efficiency for the more insoluble chromate compounds.

3. Sampling considerations

Reduction of Cr(VI) can occur by reaction with many of the polymeric materials from which filters used for air sampling are manufactured. Additionally, unreacted reagents and/or oligomers in the filter materials may also react with sampled Cr(VI) compounds and result in low recoveries. Careful selection of the filter medium used for collecting Cr(VI) is therefore of paramount importance; it is imperative that the filter material does not react with Cr(VI). Cellulosic filters and glass fiber filters containing binders are ordinarily unsuitable, as these filter types can lead to significant reduction of Cr(VI). Filter materials that are generally acceptable for sampling of airborne Cr(VI) include polyvinyl chloride (PVC), polyvinyl fluoride (PVF), polytetrafluoroethylene (PTFE), PVC- and PVF-acrylic copolymers, and quartz fiber filters. However, even filters comprised of these media should in any case be tested before use; for example, some PVC filters have been found to cause reduction of Cr(VI).[45]

Apart from potential reaction with the filter media, Cr(VI) can also be reduced to Cr(III) on the sample filter by reaction with other substances found in workplace air. For instance, Cr(VI) can react with dust containing oxidizable material such as metal from grinding operations, organic particulate matter, *etc.* This can be particularly problematic when measuring Cr(VI) in chromic acid mists,[46] because Cr(VI) is easily reduced in an acidic environment. Plasticizers in the sampler could also cause unwanted Cr(VI) reduction, so it is clearly desirable that the filter housing (besides the filter itself) be chemically inert to Cr(VI) reduction.

When sampling chromic acid mist, there is an advantage if the oxidizing potential of Cr(VI) is lowered by impregnating the filter with alkali. For example, this can be accomplished by soaking the filters in sodium hydroxide solution and then allowing the filters to dry before they are used for sampling.[46] This lessens the tendency of Cr(VI) to react with organic compounds in the filter media and/or reducing agents and dust present in the sampled air.[27] The alkaline medium might also improve sample stability if the sampled material is highly acidic. Filter materials such as PVC and PTFE can be unsuitable for alkali treatment since they are hydrophobic and are therefore not easily wetted. PVF and PVF-acrylic copolymer membrane filters have been found to have adequate wettability when soaked in NaOH solution. Impregnation of the filter with alkali is recommended in circumstances such as sampling chromic acid mist, but it is not a perfect solution to what is often an intractable problem.

Another alternative for ameliorating sample instability is to perform on-site analysis in the field.[47,48] While on-site analysis cannot prevent instantaneous reduction of Cr(VI) that may take place during sampling, field measurement can minimize longer-term reduction which could otherwise occur on the filter during sample transport and storage.[47] Besides filters, air sampling using impingers or bubblers can be considered for capturing highly reactive aerosols.[49–52] Unfortunately impingers and bubblers are not useful for personal sampling, and they often give poor sampling recoveries.[53] However, impinger/bubbler trains can prove beneficial for area sampling of Cr(VI) in reactive workplace aerosols.[49,50]

4. Sample preparation issues

4.1 Oxidation of Cr(III)

The use of a strong alkaline buffer for the dissolution of Cr(VI) compounds in air filter samples has been found to result in the oxidation of Cr(III) species.[54] The chemical behavior of Cr(III) ions in alkaline solution is expressed by:

$$Cr^{3+} + 3OH^- \leftrightarrow Cr(OH)_3$$

$$Cr(OH)_3 + OH^- \leftrightarrow [Cr(OH)_4]^-$$

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

$$[Cr(OH)_4]^- \rightarrow CrO(OH) + H_2O + OH^-$$

Hence, an increase in alkalinity will decrease the tendency towards decomposition of the complex. Oxidation by air of the hydroxo complex was suggested according to:[54]

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

During sample digestion, the hydroxo complex is involved in both of the previous reactions: (a) decomposition and (b) oxidation. The former process is the most favorable, but when the alkalinity of the solution is increased, decomposition of $[Cr(OH)_4]^-$ is suppressed and more Cr(VI) can be formed by oxidation. This oxidation can be counteracted by the addition of magnesium hydroxide, which forms a precipitate that adsorbs the hydrous chromium(III) oxide, CrO(OH).[54] Hence decomposition is favored and oxidation is minimized. It should also be noted that $[Cr(OH)_4]^-$ decomposes more readily at higher temperatures, so extraction at lower temperature is preferred.

The recommendation to use magnesium hydroxide to prevent air oxidation of Cr(III) species was subsequently adopted by the US Occupational Safety and Health Administration (OSHA) when that agency promulgated a new method for determining airborne Cr(VI).[55] In its method for determining Cr(VI) in workplace air, the US National Institute for Occupational Safety and Health (NIOSH) opted to eliminate air oxidation of Cr(III) by degassing the extraction solution with pure nitrogen, and by purging the headspace above the solution with N_2 throughout the extraction procedure.[56] However, it is not ordinarily necessary to take measures to prevent air oxidation. The effect of oxidation by O_2 in air is only of importance if there is a significant concentration of Cr(III) in the sample solution, if the Cr(VI) concentration is low (yet still significant in relation to the limit value or action level of concern), and if the extraction conditions are favorable for oxidation (*i.e.*, high temperature and alkalinity).

In addition to oxidation by O_2 from air, Cr(III) can theoretically be oxidized to Cr(VI) by redox reactions with other substances found in workplace atmospheres. An example is manganese dioxide,[57] which is present in many welding fumes. Like air oxidation, if chemical oxidation *via* redox reaction does occur, it will tend to do so to a greater extent at higher temperatures. To reiterate, these unwanted redox processes involving dissolved Cr(III) species can be protected against by the addition of magnesium hydroxide (to form precipitates which adsorb hydrous chromium(III) oxide),[54,55] or by degassing the solution.[56]

Other alkaline extraction solutions have been used for the dissolution of Cr(VI) compounds. Ammonium sulfate–ammonium hydroxide has been observed to significantly decrease oxidation of Cr(III) in fly ash samples; this advantageous development was attributed to the formation of a kinetically stable hexa-coordinated complex, $[Cr(NH_3)_6]^{3+}$.[58] Use of an ammonium sulfate–ammonium hydroxide extraction buffer for extraction of Cr(VI) from workplace air filters and other samples has also been described.[47,48] However, it has been discovered that this buffer is not caustic enough for effective extraction of Cr(VI) from the insoluble chromate compounds, *i.e.*, lead chromate and barium chromate.[59] These solubility issues regarding Cr(VI) compounds are discussed in greater detail below.

4.2 Extraction of soluble Cr(VI) compounds

Owing to differences in toxicity due to solubility considerations, there is increasing interest in the ability to separately determine soluble Cr(VI) compounds. Ultra-pure water,[43,60–65] 0.5 M sulfuric acid,[54,55] sodium acetate buffer,[39] and 1% sodium carbonate solution[54] have been used to extract soluble Cr(VI) compounds, but none of these extraction solutions is entirely satisfactory for this purpose. Because of pH considerations discussed above, extractions with 0.5 M sulfuric acid or sodium acetate (pH $\sim$ 4) will give low results for soluble Cr(VI) species if the samples contain substances that can reduce Cr(VI), notably Fe(II). This is also a concern for extraction with water. Extraction with 1% Na_2CO_3 has been used to overcome problems of extraction with water or 0.5 M H_2SO_4, because using an alkaline extraction solution reduces the potential for Cr(VI) to undergo redox reaction with, for example, Fe(II). However, 1% Na_2CO_3 solution may not strictly determine only water-soluble Cr(VI), as this medium might be expected to dissolve insoluble Cr(VI) to some extent. The use of an ammonium sulfate–ammonium hydroxide buffer has been proposed as an alternative medium for the extraction of soluble forms of Cr(VI).[65] This mixture offers the stabilizing effects of a slightly basic buffer (pH $\approx$ 8). While it is expected that quiescent leaching with ammonium sulfate–ammonium hydroxide would be effective for the dissolution of soluble Cr(VI) compounds, interlaboratory performance data supporting this contention are as yet lacking.

4.3 Dissolution of insoluble Cr(VI) compounds

Insoluble forms of Cr(VI) (as represented by lead chromate and barium chromate) are completely dissolved by the more alkaline carbonate buffer media (*i.e.*, 3% sodium carbonate–2% sodium hydroxide) when hotplate digestion is employed (Table 2). Ultrasonic extraction in this buffer system yields less than quantitative recovery for barium chromate, but gives good results for lead chromate (Table 2). In published national and standard methods, hotplate extraction using 3% Na_2CO_3–2% NaOH is the most commonplace method prescribed for the dissolution of insoluble chromate compounds in workplace air samples.[27,28,51,54,56,60,66,67] Carbonate buffers of differing strengths are recommended by OSHA for the dissolution of insoluble chromates in different types of collected air samples, *e.g.*, welding fume *vs.* chromate paint aerosols.[55] These techniques are included as optional dissolution procedures for insoluble chromate compounds in newly promulgated international voluntary consensus standards.[66,67]

4.4 Dissolution of sparingly soluble Cr(VI) compounds

Sparingly soluble forms of Cr(VI) (as represented by strontium chromate) are effectively dissolved in the 0.05 M ammonium sulfate–0.05 M ammonium hydroxide buffer, whether hotplate digestion or ultrasonic extraction is used (Table 2).[68,69] However, this extraction buffer is not effective for dissolving insoluble Cr(VI) species (Table 2): note that low recoveries are obtained for barium chromate, and that lead chromate remains undissolved. Nevertheless, sparingly soluble forms of Cr(VI) can be encountered in a number of workplace air environments, *e.g.*, spray painting, leather tanning, and certain welding operations. Hence, the 0.05 M $(NH_4)_2SO_4$–0.05 M NH_4OH extraction buffer can prove useful in situations where it is known that no insoluble Cr(VI) compounds would be present in the test atmosphere. For instance, a NIOSH field method employing ultrasonic extraction in $(NH_4)_2SO_4$–NH_4OH buffer has recently been promulgated.[71] Both ultrasonic extraction and hotplate digestion in either buffer system (*i.e.*, 3% Na_2CO_3–2% NaOH or 0.5 M $(NH_4)_2SO_4$–0.5 M NH_4OH) have been shown to give quantitative recoveries from a certified reference material (CRM), Institute for Reference Materials and Measurements (IRMM) CRM 545[47,48] (Cr[VI] in welding dust loaded on filters[72,73]). This CRM contains both soluble and sparingly soluble Cr(VI).

4.5 Recommendations on extraction media

Given the above considerations, some general recommendations regarding which extraction media to use for different purposes can be made. For the determination of water-soluble Cr(VI) in air filter samples, it is ordinarily recommended to use a buffer system of $(NH_4)_2SO_4$–NH_4OH for extraction purposes, since extraction of chromium compounds in pure water has been shown to be problematic. If it is desired to directly determine total Cr(VI) in workplace air samples, the Na_2CO_3–NaOH buffer is recommended for extraction purposes if the presence of insoluble forms of Cr(VI) is suspected. It is

Table 2 Effectiveness of extraction procedures for the dissolution of representative Cr(VI) compounds of varying solubility[48,59,68,69,70]

	Recovery of Cr(VI) (%, m/m)[a]			
Extraction procedure & alkaline buffer	K_2CrO_4[b]	$SrCrO_4$[c]	$BaCrO_4$[d]	$PbCrO_4$[d]
Hotplate Digestion:				
0.05 M $(NH_4)_2SO_4$–0.05 M NH_4OH	95 ± 1	99 ± 1	61 ± 6	(0.1)[e]
3% (m/v) Na_2CO_3–2% (m/v) NaOH	98 ± 2	105 ± 2	111 ± 10	104 ± 2
Ultrasonic Extraction:				
0.05 M $(NH_4)_2SO_4$–0.05 M NH_4OH	96 ± 12	99 ± 3	29 ± 1	(0.1)[e]
3% (m/v) Na_2CO_3–2% (m/v) NaOH	93 ± 4	102 ± 3	63 ± 20	97 ± 6

[a] (± values are standard deviations [$n \geqslant 6$]). [b] Water-soluble. [c] Sparingly soluble. [d] Insoluble. [e] (Below limit of quantitation).

reiterated that using N_2 or $Mg(OH)_2$ to prevent air oxidation of Cr(III) should be considered when using the Na_2CO_3–NaOH method. However, if it is known that no insoluble chromate compounds are present in the test atmosphere, use of the $(NH_4)_2SO_4$–NH_4OH buffer for extraction can be effective for the dissolution of total Cr(VI) species.

Separate determination of soluble and insoluble forms can be done by first extracting with $(NH_4)_2SO_4$–NH_4OH buffer to determine soluble Cr(VI), and subsequently using a buffer solution of Na_2CO_3–NaOH to dissolve insoluble chromates. Total Cr(VI) content can then be determined by summing the results obtained from the separate soluble and insoluble Cr(VI) analytical processes.

4.6 Extraction methods prescribed by the international organization for standardization

Extraction methods for Cr(VI) compounds of varying solubility have been prescribed by the International Organization for Standardization (ISO) in a Draft International Standard (DIS);[66] these procedures are outlined below.

4.6.1 Extraction of soluble Cr(VI). The ISO/DIS method prescribed for the determination of soluble Cr(VI) permits the use of either deionized water or ammonium sulfate–ammonium hydroxide buffer solution for extraction. However, several issues should be considered when deciding which extraction solution to use:

(1) The two extraction methods do not necessarily give equivalent results, as the $(NH_4)_2SO_4$–NH_4OH buffer solution should dissolve sparingly soluble Cr(VI) species more effectively than would plain water. Yet if it is desired to measure only water-soluble Cr(VI) but not sparingly soluble Cr(VI) compounds, extraction of air filter samples with water is the obvious choice.

(2) Extraction with water could yield low results for soluble Cr(VI) if the samples contain substances that can reduce Cr(VI), *e.g.*, Fe(II). Therefore, use of the $(NH_4)_2SO_4$–NH_4OH extraction solution is recommended when analyzing samples that could contain metals that can reduce Cr(VI), *e.g.*, welding fume samples.

(3) If it is believed that only soluble Cr(VI) compounds are present in the test atmosphere, and there is concern that the candidate extraction method could give biased results for soluble Cr(VI), an alternative approach is to determine total Cr(VI) (using either Na_2CO_3–NaOH or $(NH_4)_2SO_4$–NH_4OH extraction buffer) and assume that all of the Cr(VI) measured is in the soluble form.

4.6.2 Dissolution of insoluble Cr(VI). The ISO/DIS method prescribed for the determination of insoluble Cr(VI) compounds permits the use of either hotplate digestion or ultrasonic extraction using 3% Na_2CO_3–2% NaOH solution. However, the following issues should be considered when deciding which extraction method to use:

(1) If soluble Cr(III) compounds are present in the sample, they might be oxidized to Cr(VI) during dissolution in 3% Na_2CO_3–2% NaOH solution, especially when using the hotplate method, thereby giving spuriously high Cr(VI) results. So if there is a possibility for the presence of soluble Cr(III) in the test sample, it is preferable to use ultrasonic extraction rather than hotplate extraction, as oxidation of Cr(III) is less likely to occur at the lower extraction temperature involved.

(2) If measurements are required only for comparison with a limit value for insoluble or total Cr(VI) compounds, soluble Cr(VI) would not normally be separately determined. However, if soluble Cr(III) species could be present in the test atmosphere, and an ultrasonic bath is not used, the soluble Cr(VI) extraction method could be applied prior to hotplate extraction of insoluble Cr(VI) (even if there is no applicable regulatory exposure limit for soluble Cr[VI]). In this way, soluble Cr(III) compounds would be removed from the sample before the insoluble Cr(VI) method is applied.

(3) An alternative strategy to circumvent a possible positive bias due to Cr(III) conversion is to use magnesium hydroxide as a precipitation reagent to prevent air oxidation of soluble Cr(III), as described in the OSHA method.[55] Yet another technique for minimizing oxidation of soluble Cr(III) is the removal of dissolved oxygen by degassing throughout the extraction procedure, *e.g.*, as described by NIOSH.[56]

Clearly, matrix effects can influence chromium speciation measurements,[74] and it can be extremely difficult to account for any and all potential complications arising from the sample preparation method. For example, ultrasonic extraction of certain organic matrices in carbonate buffer solution can produce peroxides, which may then induce oxidation of Cr(III) to Cr(VI).[75] As another example, filter samples spiked with soluble Cr(VI) and other soluble metal compounds, including soluble Cr(III), have been shown to react to form insoluble Cr(VI) species.[70,76] Therefore some knowledge of the composition of the source material giving rise to airborne Cr(VI) species in the workplace is desirable for choosing the best sample preparation procedure for subsequent Cr(VI) measurements.

4.6.3 Other extraction methods. Other alkaline buffers have been used effectively for extracting Cr(VI) from workplace air samples. For example, phosphate buffer has been listed as an optional extraction medium in the draft ISO method,[66] and this extraction has been prescribed in a German method for determining Cr(VI) in workplace air samples that are collected onto binder-free glass fiber filters.[77] Tris(hydroxymethyl)-aminomethane hydrochloride (Tris-HCl)–sodium hydroxide is another buffer system that has been shown to be effective for extracting Cr(VI) compounds.[48] Besides extraction of Cr(VI) compounds using phosphate solution, the standard German procedure also endeavors to eliminate potential positive biases from Cr(III) oxidation to Cr(VI) by derivatizing the trivalent species during extraction. This is accomplished *via* selective reaction of Cr(III) with pyridine-2,6-dicarboxylic acid (PDCA), which is added to the extraction buffer. While the advantage of Cr(III) derivatization is obvious, cited disadvantages are that the procedure is complicated and the required analytical apparatus is complex.[77]

5. Separation and analytical measurement techniques for airborne Cr(VI)

Separation and isolation of Cr(VI) prior to analytical measurement is necessary for many types of samples that are collected from workplace atmospheres. As discussed earlier, in some sample matrices, other metal species can act as interferences to Cr(VI) analysis. For example, in the case of Cr(VI) measurement using the DPC method, separation of Cr(VI) from sample extracts containing Fe(II) is crucial before spectrophotometric analysis is attempted. If extracted Cr(VI) is not isolated from dissolved Fe(II) prior to acidification and reaction of the hexavalent species with DPC, the acidic environment (which is necessary for the Cr(VI)-DPC reaction) would facilitate reduction of Cr(VI) by divalent iron. Obviously this unwanted redox reaction could result in low recoveries of Cr(VI).

As another example, if atomic spectrometric methods are used for analysis of sample extracts, separation of Cr(VI) is ordinarily required if Cr(III) might also be present. This is because atomic spectrometry does not differentiate between Cr(III) and Cr(VI); so if there is a possibility for both species to be present, clearly a separation step is needed prior to measurement. Due to the risk of encountering potentially interfering metals in numerous occupational settings where Cr(VI) could be encountered, Cr(VI) determination in air

Table 3 Various analytical methods for determining Cr(VI) in air samples

Sample matrix(es)	Analytical method(s)[a]	Reference(s)
Welding fume	DPC[b] (interlaboratory evaluations)	30,31
Welding fume	Selective solubilization of Cr species/DPC	43,52,54,62
Welding fume	Various (interlaboratory evaluation): IC[c]/DPC; ETAAS;[d] ICP-AES[e]; ICP-MS;[f] IDMS[g]	73
Welding dust	DPC	36
Welding dust	Selective solubilization of Cr species/DPC; voltammetry	37
Welding	Anion-exchange chromatography/ETAAS	78
Plating mist	DPC	29,46
Plating mist	Precipitation of Cr species/X-ray spectrometry	79
Acid mist, welding fume	DPC; AAS[h]	39
Acid mist, welding fume	Selective solubilization of Cr species/DPC	59
Metallic aerosols	DPC; AAS	38
Paint aerosols	IC/conductivity detection; ICP-AES	45
Spray painting, sanding, welding dust, etc.	Anion exchange solid-phase extraction/DPC (field-portable)	47,48,69
Ambient air	ICP-MS	80
Aerosols	IC/DPC	23,49,50,68,69
Aerosols	IDMS; IC/DPC	81
Aerosols	Anion exchange/IDMS	82
Aerosols	Automated anion exchange/DPC (portable)	83
Air filters	FIA[i]/DPC	34
Air filters	Liquid membrane extraction/DPC	84

[a](Not all analyses used a separation/isolation scheme). [b]Spectrophotometry by1,5-diphenylcarbazide method. [c]Ion chromatography. [d]Electrothermal atomic absorption spectrometry. [e]Inductively coupled plasma – atomic emission spectrometry. [f]Inductively coupled plasma – mass spectrometry. [g]Isotope dilution mass spectrometry. [h]Atomic absorption spectrometry. [i]Flow-injection analysis.

samples often necessitates a separation scheme upstream of the analytical measurement. Separation procedures can also help to eliminate spectral interferences from other metal species that might be present in the test sample.

The most widely used technique for the separation and isolation of Cr(VI) in environmental samples is ion chromatography (IC). Indeed, most of the standard methods which have been promulgated for measuring airborne Cr(VI) specify IC for separation purposes.[55,56,60,66,67,77] As mentioned earlier, Cr(VI) is easily separated from other metal species because it is anionic at pH < 10, while other metal species, including Cr(III), exist as cations in slightly basic buffer. Other separation techniques that have been used successfully for isolating Cr(VI) from extracted air samples include anion exchange, solid-phase extraction, precipitation, and miscellaneous extraction methods (Table 3).

A wide variety of analytical finishes for the measurement of Cr(VI) in test samples has been published; some examples of these techniques are presented in Table 3. The popular 1,5-diphenylcarbazide spectrophotometric method has been used widely for routine applications. Yet a variety of other methodologies, including spectrometric and electroanalytical techniques, have also been applied to the determination of Cr(VI) in air samples. Atomic spectrometric methods such as electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) have been used extensively, as these instrumental techniques offer detection limits that are low enough for trace chromium measurements. However, flame atomic absorption spectrometry (FAAS) does not generally offer low enough detection limits for Cr(VI) determination when considering applicable exposure limit values.

Very low instrumental detection limits are attainable with inductively coupled plasma-mass spectrometry (ICP-MS), which has been used for Cr(VI) ambient air monitoring.[80] But ICP-MS has not yet seen wide use for workplace air measurement of Cr(VI). The high capital cost of ICP-MS (compared to, *e.g.*, ETAAS and ICP-AES) tend to relegate this technique to more specialized work than routine measurements of chromium species in atmospheric samples. Yet as action levels for airborne Cr(VI) compounds become lower, highly sensitive methods such as ICP-MS may become used more often.

Another interesting development has been the use of isotope dilution mass spectrometry (IDMS), which has been applied to Cr(VI) speciation in welding fume samples prepared for the development of a certified reference material.[73] IDMS and related isotopic labeling techniques enable the investigator to track the fates of labeled chromium species of different valences engaging in redox reactions.[81,82] In turn, IDMS can be used to correct for biases resulting from interspecies transformations during sample preparation. For example, experiments have been conducted by spiking samples with known concentrations of trivalent and/or hexavalent ^{53}Cr, and using thermal ionization mass spectrometry[81] (TIMS) or ICP-MS[82] for detection of chromium isotopes. It is thus possible to track the fate of individual chromium species (*i.e.*, ^{52}Cr and ^{53}Cr) engaging in redox reactions during sample preparation processes. It has been shown definitively that Cr(III) can be oxidized to Cr(VI) under conditions of hot alkaline extraction. Furthermore, IDMS has confirmed that Cr(VI) can be reduced to Cr(III) in acidic media and in the presence of reducing agents. IDMS techniques to correct for analytical biases arising from these species transformations have been developed.[81,82] Realistically, however, IDMS is mainly useful for research studies, since for most service analytical laboratories it is not a rapid, affordable nor user-friendly technique for routine Cr(VI) measurements.

Certainly atomic spectrometric techniques as well as X-ray methods can be used to measure total chromium concentrations in air samples, and this is often done in cases where it is assumed that all of the chromium species collected exist in the hexavalent form in the sampled atmosphere. However, as mentioned earlier, chemical speciation ordinarily requires a separation step prior to measurement by atomic spectrometry. Electroanalytical measurements can sometimes obviate the need for chemical isolation of Cr(VI) prior to analysis, but higher sample throughput is usually possible with spectrophotometry by the DPC method, and/or by atomic spectrometric measurement methods such as ETAAS and ICP-AES.

6. Speciation techniques for Cr(VI) in environmental matrices and related media

While the focus of this article has to do with the determination of Cr(VI) in workplace atmospheric samples, it is relevant to

Table 4 Example methods for Cr(VI) measurement in non-atmospheric samples

Matrix(es)	Analytical method(s)[a]	Reference(s)
Tanned leather	DPC[b]	8
Paint chips, fly ash, soils, *etc.*	FIA[c]/DPC	34,85,86
Soils	IC[d]/DPC	63,74
Acid-washed sand	Liquid membrane extraction/DPC	84
Soils, sediments	Voltammetry	87–89
Cement	Various (interlaboratory evaluation): DPC, AAS,[e] ICP-AES[f]	90
Metal oxides	Solid-phase extraction/AAS	91
Steel, coatings	Soft X-ray spectrometry	92
Cr ore residue, fly ash, *etc.*	IDMS[g]	93,94
Water	Anion exchange/IDMS	95
Water	Solid-phase extraction/ultraviolet detection	96
Water	Preconcentration/DPC	97–99
Waste water	Anion exchange/DPC	100
Aqueous samples	FIA/fluorimetric detection	101,102
Aqueous samples	IC/ICP-AES	103
Aqueous samples	IC/ICP-MS[h]	104–108
Aqueous solutions	Voltammetry	87,109–111
Aqueous solutions	FIA/AAS	112–114
Aqueous solutions	FIA/electrode sensor array	115
Aqueous solutions	Chelation/HPLC[i]/diode-array detection	116
Aqueous solutions	Reflectance (DPC colorimetry)	117,118
Aqueous solutions	Laser photoacoustic spectroscopy	119,120

[a](Not all analyses used a separation/isolation scheme). [b]Spectrophotometry by 1,5-diphenylcarbazide method. [c]Flow-injection analysis. [d]Ion chromatography. [e]Atomic absorption spectrometry. [f]Inductively coupled plasma – atomic emission spectrometry. [g]Isotope dilution mass spectrometry. [h]Inductively coupled plasma-mass spectrometry. [i]High-performance liquid chromatography.

briefly discuss Cr(VI) measurements in other sample matrices, especially environmental media. Potential exposures to workers can result from the disturbance of environmental media and/or industrial products that may contain chromates in significant concentrations. As another consideration, chemical speciation methods developed for the analysis of liquid or solid environmental and/or industrial samples can often be modified for use in the analysis of atmospheric samples. Studies of chemical speciation in environmental matrices and other media might be invaluable in our efforts to understand the chemistry occurring during workplace air sampling and analysis. Also, methods developed for the determination of Cr(VI) in non-atmospheric samples can often be modified for use for chromium speciation in workplace air samples.

Examples of analytical methods that have been used for the determination of Cr(VI) in a variety of sample matrices (non-atmospheric) are summarized in Table 4. As for airborne particulate samples, alkaline digestion has become a widespread standard technique for extracting Cr(VI) from solid environmental matrices,[121] *e.g.*, solid waste.[122] Also, use of the DPC measurement method for environmental samples is common as well.[123] A variety of methods have been used for separation of trivalent and hexavalent species (Table 4). Of these separation techniques, IC is undoubtedly the most popular method for routine speciation analysis of environmental and other samples, not only for chromium species but for other metal ions as well.[124] Flow-injection analysis (FIA) methods have been developed, for instance FIA using on-stream sample preparation with photometric,[85,86] fluorimetric,[101,102] or electrochemical[115] detection. FIA techniques offer possibilities for field-portable measurement of Cr(VI).

As in samples obtained from air, species transformations can occur during preparation of (non-atmospheric) environmental and related samples, and investigations of Cr(III) oxidation and/or Cr(VI) reduction have been made possible by using IDMS (with ICP-MS detection).[93–95] Indeed, biases from Cr(III) oxidation during extraction have been shown by IDMS studies to exceed 150% in some solid samples.[94] Very low detection limits are afforded by using techniques such as ICP-MS, which enable the analyst to measure trace quantities of specific isotopes, *e.g.*, ^{50}Cr, ^{52}Cr and ^{53}Cr. Indeed, ICP-MS has proven especially useful for trace measurement of chromium species in liquid samples.[104,105] Unlike atmospheric sampling, however, environmental samples are ordinarily less prone to complications from transformations of chromium species occurring during sample collection. A technique for stabilizing chromium species during extraction by complex formation has been investigated;[125] this method may offer a useful procedure for preventing Cr(III)/Cr(VI) species transformations during sample preparation.

7. Concluding remarks

Chromium speciation has received considerable attention recently, owing to the need for reliable sampling and analytical methods for determining Cr(VI) in workplace air and related samples. Recent efforts to standardize measurement procedures have focused on methods that offer features such as: (1) low detection limits; (2) high selectivity; (3) minimization of species transformation due to redox reactions; (4) robustness and ease of use; and (5) comparatively low cost. Advantages and limitations of the more widely used techniques for measuring Cr(VI) have been highlighted here.

The availability of representative Cr(VI)-containing CRMs, as well as proficiency testing schemes for Cr(VI), would also provide better means for traceability and analytical performance evaluation. However, performance evaluation materials are expensive to produce, especially when considering Cr(VI) compounds, which are unstable in numerous matrices of interest. Moreover, participation in proficiency analytical testing can be cost-prohibitive for many laboratories. In any case, it is hoped that the promulgation of new voluntary consensus standards for the determination of airborne Cr(VI) will enable better comparability of analytical results between laboratories. Where standardized methods cannot provide the analyst with all desired information (*e.g.*, results regarding conversion of trivalent and hexavalent forms), the use of more specialized (albeit higher cost and/or complexity) techniques can be investigated.

8. List of Abbreviations

AAS: Atomic absorption spectrometry
ACGIH: American Conference of Governmental Industrial Hygienists

CEN: *Comité Européen de Normalisation* (European Committee for Standardization)
CRM: Certified reference material
DIS: Draft International Standard
DNA: Deoxyribonucleic acid
DPC: 1,5-Diphenylcarbazide
EPA: Environmental Protection Agency (USA)
ETAAS: Electrothermal absorption spectrometry
FAAS: Flame atomic absorption spectrometry
FIA: Flow-injection analysis
HPLC: High-performance liquid chromatography
HSL: Health and Safety Laboratory (UK)
IC: Ion chromatography
ICP-AES: Inductively coupled plasma-atomic emission spectrometry
ICP-MS: Inductively coupled plasma-mass spectrometry
IDMS: Isotope dilution mass spectrometry
INRS: *Institut National de Recherche et de Sécurité* (France)
IRMM: Institute for Reference Materials and Measurements (Belgium)
ISO: International Organization for Standardization
NIOSH: National Institute for Occupational Safety and Health (USA)
NIWL: National Institute for Working Life (*Arbetslivsinstitutet*, Sweden)
OSHA: Occupational Safety and Health Administration (USA)
PDCA: Pyridine-2,6-dicarboxylic acid
PTFE: Polytetrafluoroethylene
PVC: Polyvinyl chloride
PVF: Polyvinyl fluoride
TIMS: Thermal ionization mass spectrometry
TLV: Threshold Limit Value®
Tris-HCl: Tris(hydroxymethyl)aminomethane hydrochloride
TWA: Time-weighted average

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