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A simple analytical technique for the determination of hexavalent chromium in welding fumes and other complex matrices

by EBBE THOMSEN, M.Sc.,¹ and RICHARD M. STERN, Dr.rer.Nat.²

THOMSEN, E. & STERN, R. M. A simple analytical technique for the determination of hexavalent chromium in welding fumes and other complex matrices. *Scand. j. work environ. & health* 5 (1979) 386—403. A systematic study of analytical methods for the determination of hexavalent chromium showed that currently existing techniques are unsatisfactory when used with welding fumes, the s-diphenylcarbazide method proposed by the U.S. National Institute for Occupational Safety and Health permitting less than 1 % recovery of hexavalent chromium from synthetic welding fumes of known composition. A new (carbonate leaching) technique is proposed which permits better than 80 % recovery of both soluble and insoluble chromium (VI). This technique is then used as part of a general method for the determination of total chemical composition as distributed among sample fractions of different solubility. The method is specifically designed for use in the analysis of small samples and is especially suitable for the routine evaluation of health risks as found in the work environment.

Key words: autoredox systems, chemical analysis, chromium, hexavalent chromium, industrial hygiene, welding fumes.

Chromium (Cr) and chromium compounds frequently occur in the work environment and are associated with processes such as the welding and grinding of stainless steel, chrome plating, tanning, wood preserving, painting, and pigment production. Hexavalent chromium (Cr⁺⁶) compounds are considered to be particularly dangerous, primarily because of the associated risk of allergic reaction and cancer (16).

The analysis of Cr⁺⁶ according to the s-diphenylcarbazide (DPC) method (1) and all other previously used techniques is

often made uncertain by significant interferences from organic components and redox systems in the actual matrix being investigated. This report presents a method for the uncomplicated determination of total Cr⁺⁶ content in complex matrices for which other methods have been demonstrated to be inappropriate.

The toxicity of certain chromium compounds has been established for at least 150 years (4). Trivalent chromium (Cr⁺³) is considered to be of very low toxicity, presumably because of the relatively low membrane permeability of this ion. Cr⁺⁶ compounds on the other hand exhibit a wide range of toxic potency, presumably because of the ease with which the Cr⁺⁶ ion can be absorbed in the alimentary canal and respiratory tract and transported

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across cell membranes. There is at present some degree of uncertainty concerning the carcinogenic properties of Cr^{+6} , primarily because of the difficulty in interpreting human epidemiologic data based on mixed exposure to different types of chromium compounds typical for most industrial situations. Although it has been shown that water-soluble Cr^{+6} is a mutagen in short-term in vitro screening tests (10, 15, 18, 20) and a wide range of chromium compounds has produced injection site tumors in experimental animals (17), the NIOSH (National Institute for Occupational Safety and Health) criteria document for recommended exposure levels for Cr^{+6} (17) and recent, well-documented epidemiologic studies (7, 12, 13) can be interpreted (21) as strongly indicating that Cr^{+6} compounds of intermediate solubility are to be considered as suspected potent carcinogens. Highly soluble and highly insoluble chromium may have a relatively low carcinogenic potential for humans (7, 26) although the absence of good criteria for defining or identifying individuals exposed to adequately high doses may lead to a general masking effect. For self-evident reasons, the difficulty in measuring insoluble hexavalent chromium in complex substances introduces considerable uncertainty concerning the actual nature of the chromium content of a number of industrial exposures, and this situation increases the difficulty of interpreting epidemiologic data.

It has been established that Cr^{+6} compounds are biologically active, mutagenic and apparently, as determined by their solubility, carcinogenic, although at present an assignment of carcinogenicity as a function of solubility is still somewhat speculative. This situation leads to considerable uncertainty in the strategies to be used in evaluating and reducing risks to chromium exposure in the work environment, since there is a significant difference in the permitted hygienic levels for exposure to toxic and to carcinogenic material. Threshold limit values (TLVs) for toxic material are typically set at concentrations which experience has shown to result in no observable clinical effects [e.g., $500 \mu\text{g}/\text{m}^3$ for Cr^{+2} and Cr^{+3} compounds calculated as Cr, and $100 \mu\text{g}/\text{m}^3$ for Cr^{+6} (non-carcinogenic) calculated as chromic oxide (CrO_3)], while those for carcinogens are

presently administratively defined as zero, practically determined by the detection limit ($1 \mu\text{g}/\text{m}^3$ for carcinogenic Cr^{+6}) in order to avoid the current controversy concerning carcinogenic potential at low concentrations.

Welding is a common nonmechanized process whereby copious amounts of fume can be produced locally at high concentrations which present a potentially high hygienic risk. More than 95 % of the fumes are respirable (19), and as much as 38 % of the chromium content is retained after being inhaled (2). Stainless steel fume particles have been identified in lung tissue (25), and magnetic welding fumes of the order of 1–2 g [typically containing 40 % magnetite (Fe_3O_4) from mild steel welding] have been found deposited in the respiratory tract of older welders (11). The chemistry of welding fumes is extremely dependent on the welding process, the type of materials used, and the welding parameters chosen. Welding on stainless and other high alloy steel can produce fumes containing up to 25 % chromium, distributed in all possible oxidation states and solubilities. It should also be pointed out that another potential carcinogen, nickel, can be present in concentrations of over 50 % in fumes from certain processes and should therefore be considered in any potential risk assessment.

An evaluation of the risk associated with the chromium content of a particular work environment requires knowledge of the possible compounds contained therein and their respective toxicity and therefore equally requires the existence of analytical techniques to determine quantitatively the composition of the matrix of interest. Welding fumes are a class of material which contains Cr^{+6} in unpredictable forms in a complex matrix and for which a quantitative analysis has therefore been impossible, especially with respect to the determination of the insoluble Cr^{+6} content. In particular, calculated hygienic exposure or permitted occupational exposure levels and the relative values for different welding processes and process parameters (i.e., voltage and current) based on the chromium content have been found to depend on the analytical method chosen for the Cr^{+6} determination. In the following discussion, a simple method for the

routine determination of Cr^{+6} in welding fumes is presented, together with a procedure for determining total elemental composition (including Cr^{+6}) as a function of solubility (i.e., fractionization) for use with fume quantities typical of normal practice in industrial hygiene situations. It is also shown that the currently recommended procedure for Cr^{+6} determination, the s-diphenylcarbazide technique of NIOSH (17), is not suitable for use with welding fumes.

ANALYSIS OF HEXAVALENT CHROMIUM IN THE PRESENCE OF REDOX SYSTEMS

Determination of hexavalent chromium in welding fumes according to known methods

Matrix determined errors. Welding fumes are complicated from both a physical and chemical point of view, and they have been described in detail in terms of analytical chemistry, particle size distribution, and particulate morphology for a series of common welding processes, each of which produces characteristic fumes which can be defined within a wide but finite range of parameters (22, 23). For mild (i.e., unalloyed) steel welding, the major component of the fume is Fe_3O_4 , typically magnetite in crystalline form, while a wide range of other elements appear in often unknown compounds and complexes. Fumes which contain chromium are usually produced by the welding of stainless steels, and they contain, by the nature of the alloys used, iron, nickel, vanadium and other elements which can directly interfere with the Cr^{+6} determination when it is carried out by the standard DPC method (1). The isolation and extraction of all chromium, followed by a specific determination of chromium content, e.g., by means of atomic absorption spectrophotometry, can be used to eliminate these interferences. Such a method is typically described in the literature for standard methods (3). A method using electron spectroscopy for chemical analysis (ESCA) has been recently proposed for the determina-

tion of Cr^{+6} in welding fumes (14), but it appears to have the significant disadvantage of both interference from other chromium oxidation states and a primary sensitivity to the chemical composition of the surface layer (of the order of 20 Å) of the fume particles and hence is inappropriate for use on fumes for which homogeneity has not previously been established; the equipment and personnel for such analyses are also not universally available.

Wet chemical analysis of insoluble and slightly soluble chromates normally requires dissolution at a low pH as the absolute solubility of chromate compounds increases with increasing acid concentration because of the low value of the second ionization constant (K) of chromic acid ($K' \simeq 2 \times 10^{-1}$, $K'' \simeq 4 \times 10^{-7}$):

In addition to the interferences which directly affect Cr^{+6} determination, there exists the risk of change in the oxidation state of the chromium ions during sample preparation with wet chemical methods, which leads to a measured Cr^{+6} content which does not correspond to the original composition of the sample. Because of the oxidizing potential of Cr^{+6} and the latent reducing potential of the magnetite present in welding fumes, a change in the oxidation state of the chromium present in the fumes is quite likely. A determination of the Cr^{+6} content can be either too low or too high, depending on the relative rates of the following reactions:

Variation in the oxidation state during analysis will depend on the relative acid concentration and presence of oxidizing or reducing compounds; thus the solubility of the fume components and the pH used will establish the extent to which the measured Cr^{+6} content agrees with the actual composition of the fume. The relative solubilities as a function of pH for several compounds which appear in welding fumes and play a role in equations b, c and d are

shown in fig. 1 [values from Freier (8, 9)]. It can be seen from fig. 1 and equations b, c and d that the analysis of slightly soluble and insoluble chromates in welding fumes dissolved under highly acidic conditions will be significantly affected by large amounts of Fe^{+2} from the magnetite present, the low pH enhancing the reduction of Cr^{+6} . It can therefore be expected that relatively insoluble chromates (with low TLVs) will be found in concentrations which are significantly lower than their actual occurrence in the fumes.

Analysis of hexavalent chromium/chromium in synthetic welding fumes. Synthetic welding fumes having a known chemical composition were analyzed for Cr^{+6} /chromium as a function of their composition for the purpose of examining the applicability of a number of methods for Cr^{+6} determination in systems containing chromium in a range of oxidation states in different concentrations and which also contain magnetite in amounts typical for

welding fumes. Particular emphasis was placed on determining the effect of pH on the recovery of highly soluble Cr^{+6} [in the form of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)] and insoluble Cr^{+6} [in the form of lead chromate (PbCrO_4)].

The solid samples were prepared for analysis by heating to the boiling point with the appropriate solvent, as recommended by three common techniques — (a) 0.5 n sulfuric acid [as recommended by NIOSH (17)], (b) a sodium acetate buffer [as suggested by Blomquist (5)], and (c) demineralized water. The filtrate was analyzed for chromium by atomic absorption, and in certain cases for Cr^{+6} by the DPC method, a single determination being made in each case. The results of the chromium and Cr^{+6} recovery, for different compositions, as a function of the preparation pH and analysis technique are shown schematically in fig. 2.

For pure, highly soluble chromate ($\text{K}_2\text{Cr}_2\text{O}_7$), there was good agreement between the Cr^{+6} content as determined by

Fig. 1. Solubilities of some possible constituents of welding fumes as a function of pH.

the DPC method and total chromium as determined by atomic absorption spectrometry (AAS), recovery being greater than 95 % independent of the solution pH. As expected, the insoluble chromate was only dissolved and could only be recovered at a low pH; for $\text{pH} > 4$ less than 10 % of the original chromium was recovered, the two methods giving identical results. With an acidic solution 75 % of the chromium was recovered with the DPC method, and 98 % by AAS.

In the presence of magnetite, less than 1 % of the insoluble chromate appeared (as Cr^{+3}) in solution, both AAS and DPC methods giving the same low value; the rest remained undissolved and hence undetected. At a low pH 98 % of the chromium could be recovered, reduced to Cr^{+3} as detected by AAS; the DPC method showed less than 1 % Cr^{+6} . Although the total chromium could be determined independently of pH by use of AAS, for the soluble chromate, in the presence of magnetite, at least 10 % of the Cr^{+6} was reduced even at

neutral pH (only 90 % being recovered by the DPC method); the Cr^{+6} was found to be completely reduced upon acid solution (essentially zero recovery with the DPC method).

In addition to the synthetic welding fumes, the analysis of which is presented in fig. 1, similar studies were made of a series of samples containing an extended range of Cr^{+6} compounds of different solubilities [calcium chromate (CaCrO_4), zinc chromate (ZnCrO_4)], together with Cr^{+3} [as chromic chloride (CrCl_3)]. The composition of the entire series of synthetic welding fumes, together with the appropriate analysis results, are presented in table 1. An examination of table 1 shows that insoluble Cr^{+6} compounds cannot be determined in synthetic welding fumes by means of the DPC method, as the presence of magnetite leads to a reduction of the dissolved Cr^{+6} by more than 99 %. It can also be seen that the solubility of chromium compounds appears to be reduced by the presence of magnetite,

Fig. 2. Chromium recovery for different sample compositions as a function of pH. Atomic absorption spectroscopy (AAS) — — —; s-diphenylcarbazide method (DPC) — — —.

presumably due to the basic character of the magnetite (in spite of the presence of the sodium acetate buffer). The presence of Cr^{+3} was not found to interfere with the Cr^{+6} determination, the Cr^{+3} appearing however in the total chromium content, as determined by the AAS method.

Nonapplicability of known analytical methods for hexavalent chromium in welding fumes. From the preceding discussion it can be concluded that the DPC method, both as recommended by NIOSH (17) or as modified by Blomquist (5), is a satisfactory technique for Cr^{+6} determination, provided direct and indirect interferences can be eliminated, and is especially useful when the sample contains only Cr^{+6} . If this is known to be the case, however, then simple AAS is as satisfactory.

In the case of complex samples such as

welding fumes which contain reducing/oxidizing substances, there is the possibility of interference from metals which form colored complexes with DPC, as well as the probability of changes in the original Cr^{+6} concentration during analysis. This latter problem is enhanced by the low pH required for the DPC reaction itself, and also by the low pH frequently required for sample solution, especially for those solutions containing chromates of low solubility (fig. 2). The presence of magnetite in most welding fume samples insures that almost all of the slightly soluble Cr^{+6} eventually dissolved will be reduced before measurement. The DPC method, as other wet chemical methods, cannot be used for Cr^{+6} determination in either welding fumes or other samples for which the necessary sample preparation liberates latent redox processes present in the matrix.

Table 1. Results of chromium analyses of synthetic welding fumes of different chemical compositions with atomic absorption spectrometry (AAS) and the s-diphenylcarbazine (DPC) method.

Sample no.	Composition				Preparation	Results			
	MeCrO ₄		CrCl ₃	Fe ₃ O ₄		AAS		DPC	
	Me	(mg Cr+6)	(mg Cr+3)	(mg)		Found (mg Cr)	Recovery (% Cr)	Found (mg Cr+6)	Recovery (% Cr+6)
1	Pb	8.7	0	0	0.5 n sulfuric acid	8.4	98	6.4	74
2	Pb	9.9	0	1,000	0.5 n sulfuric acid	9.5	96	0.1	1
3	Pb	8.1	59.0	0	0.5 n sulfuric acid	65.0	97	—	—
4	Pb	8.4	74.2	1,000	0.5 n sulfuric acid	81.0	98	—	—
5	Ca	15.5	0	0	0.5 n sulfuric acid	15.5	100	—	—
6	Zn	12.5	0	0	0.5 n sulfuric acid	12.5	100	—	—
7	K ^a	17.6	0	0	0.5 n sulfuric acid	17.4	98	—	—
8	K ^a	10.1	0	0	0.5 n sulfuric acid	10.3	102	10.1	100
9	K ^a	10.5	0	1,000	0.5 n sulfuric acid	10.2	97	0.6	6
10	K ^a	17.4	35.6	0	0.5 n sulfuric acid	51.9	98	—	—
11	Pb	8.4	0	0	Sodium acetate buffer pH 4	0.7	8	0.8	10
12	Pb	8.8	0	1,000	Sodium acetate buffer pH 4	0.06	1	0.006	0
13	Pb	3.8	0	0	Sodium acetate buffer pH 4 ^b	0.4	10	0.39	10
14	K ^a	10.3	0	0	Sodium acetate buffer pH 4	10.3	100	9.98	97
15	K ^a	9.4	0	1,000	Sodium acetate buffer pH 4	9.0	96	8.1	86
16	Pb	8.1	0	0	Demineralized water	0.72	9	0.83	10
17	Pb	8.4	0	1,000	Demineralized water	0.06	1	0.06	1
18	Pb	8.3	55.4	0	Demineralized water	50.0	78	—	—
19	Pb	9.6	64.2	1,000	Demineralized water	57.0	77	—	—
20	K ^a	9.3	0	0	Demineralized water	9.15	98	8.80	95
21	K ^a	9.7	0	1,000	Demineralized water	9.35	96	8.50	88

^a As potassium dichromate.

^b Cold extraction.

The alternative physical-chemical methods, such as ESCA, although not presenting a risk with respect to variation of the Cr^{+6} oxidation state during measurement, would appear inappropriate for routine investigations of welding fumes or for the quantitative determination of inhomogeneous samples with a low Cr^{+6} content. Thus there would appear at present to be no published technique for the routine evaluation of the Cr^{+6} risk present in common industrial exposures in general and welding fumes in particular.

Analysis of total hexavalent chromium in welding fumes

Requirements of the analytical method. An acceptable method for the determination of Cr^{+6} in welding fumes must provide for complete leaching of all Cr^{+6} from the sample matrix without liberating any latent oxidation or reduction potential and thereby permit a quantitative determination of the undisturbed original Cr^{+6} content. If used as a basis for risk evaluation in the work environment, the method must have a sufficiently low detection limit so as to permit significant measurements in typical samples containing Cr^{+6} at or below the permitted hygienic exposure levels. Furthermore, it is desirable that the technique be able to separate the Cr^{+6} detected into several intervals of varying toxicity such as might be determined by fractions of varying relative solubility.

Analytical principles. It has been demonstrated that the currently available analytical methods utilizing acidic to neutral sample preparation all suffer from the disadvantage of the reduction of a large fraction of the Cr^{+6} content of the synthetic welding fume samples tested. With alkaline leaching, however, only a very small amount of the reducing component of the welding fumes (in this case Fe^{+2}) will be liberated and in quantities insignificant when compared to Cr^{+6} , so that no reduction should take place. This phenomenon can be seen from fig. 1, which illustrates the fact that the solubility of ferro compounds at pH 11 is approximately 10^{-15} of that at pH 2. The solubility of the

Ni^{+2} , Cr^{+3} , and many other metals contained in the welding fumes will similarly disappear at a high pH. Slightly soluble or insoluble Cr^{+6} compounds which do not contain amphoteric ions will however in general be insoluble at a high pH as well.

The current work describes a method for the solution of chromates at a high pH by means of carbonate leaching, a technique which is generally used for the leaching of insoluble sulfates. The method is described by the following reaction:

In the presence of a large excess of carbonate, equilibrium is shifted quantitatively to the right, insoluble chromates becoming transformed to insoluble carbonates and dissolved chromate. The necessary carbonate excess is determined by the solubility product of the material used, since, following equation e, equilibrium is described by:

$$\frac{[\text{MeCO}_3] \cdot [\text{CrO}_4^{--}]}{[\text{MeCrO}_4] \cdot [\text{CO}_3^{--}]} = K_1 \quad (\text{f})$$

or

$$\frac{[\text{CO}_3^{--}]}{[\text{CrO}_4^{--}]} = \frac{1}{K_1} \frac{[\text{MeCO}_3]}{[\text{MeCrO}_4]} = K, \quad (\text{g})$$

where with the use of the solubility products defined by:

$$L_{\text{MeCO}_3} = [\text{Me}^{++}] [\text{CrO}_4^{--}] \quad (\text{h})$$

and

$$L_{\text{MeCrO}_4} = [\text{Me}^{++}] [\text{CO}_3^{--}], \quad (\text{i})$$

and, following equations g, h and i,

$$\frac{[\text{CO}_3^{--}]}{[\text{CrO}_4^{--}]} = K = \frac{L_{\text{MeCO}_3}}{L_{\text{MeCrO}_4}}. \quad (\text{j})$$

The entire chromate content of the sample can be expected to go into solution as soon as the carbonate concentration becomes K times the expected chromium content.

Based on the solubility products given by Freier (8, 9), the approximate K values for the conversion of lead chromate (PbCrO_4) and silver chromate (Ag_2CrO_4) are calculated to be $K_{\text{Pb}} = 1.86$ and $K_{\text{Ag}} = 1.54$. When the relatively small amounts of chromium expected to be found in welding fumes are considered, there should be no difficulty in establishing the necessary excess of carbonate required.

The preceding discussion provides the theoretical principle used in the analytical method. Because of the temperature dependence of the solubility products and equilibrium constants involved and the possibility of the formation of oxides, hydroxides, and various other basic compounds and complexes in place of carbonates, a quantitative theoretical treatment of the actual situation during analysis is extremely difficult to perform.

Procedure for determination of total hexavalent chromium by the carbonate method. Total Cr^{+6} is determined by the carbonate method as follows: (a) the sample is weighed in a beaker, (b) 50.0 ml of 7 % sodium carbonate is added, (c) the sample is warmed to boiling, (d) the sample is left to cool, (e) the precipitate is removed by filtration, and finally (f) the filtrate is analyzed directly for Cr^{+6} .

Analysis of hexavalent chromium/chromium in synthetic welding fumes by the carbonate method. Synthetic welding fumes having a wide variety of known chemical compositions were analyzed according to the carbonate method just described. Samples were produced consisting of varying amounts of chromates of different solubility (lead, calcium, zinc, silver and potassium chromate) mixed with a range of concentrations of Cr^{+3} (as CrCl_3) and Fe_3O_4 .

Some of the filtrates were also analyzed by the DPC method for Cr^{+6} . In general it was found that all the pure chromates studied were dissolved in the carbonate method and that the chromium content determined directly by AAS was identical to that expected for Cr^{+6} to within about 10 %. Large concentrations of Cr^{+3} did not interfere with the recovery. In the presence of magnetite, however, somewhat less Cr^{+6} was recovered than the amount originally contained in the samples, the recovery rate depending partly on the chromate examined and partly on the amount of magnetite present. The analysis of silver chromate appeared to show a systematic error of unknown origin that led to a recovery of 110 %. With a single exception (a zinc chromate sample containing large amounts of magnetite and Cr^{+3}), recovery was always between 75–110 % of the

original Cr^{+6} content. The systematic behavior of the Cr^{+6} recovery as a function of magnetite for different chromates is shown in fig. 3, and the results of the entire series of measurements are assembled in table 2. All measurements were made in single determinations.

DISCUSSION OF THE CARBONATE METHOD

Detection limits and recovery

The carbonate method can provide a technique for the rapid and simple determination of total hexavalent chromium in welding fumes and is, in this respect, unique when compared to other current methods. It can be used for routine measurements on standard hygienic samples (i.e., Millipore filters). At lower concentrations, the sensitivity can be increased by the use of flameless atomic absorption techniques or the use of a smaller solution volume. With low loading, as little as $0.8 \mu\text{g}$ was detected on such a filter, a level corresponding to a sample obtained under normal

Fig. 3. Recovery of lead (○), zinc (▲), cadmium (□), potassium (▽), and silver (●) chromate as a function of magnetite content.

conditions for exposure (0.8 m^3) at the proposed NIOSH limit ($1 \mu\text{g}/\text{m}^3 \text{ Cr}^{+6}$). The sensitivity, recovery, and uncertainty of the method are within the limits normally associated with measurements made in the work environment.

The influence of the carbonate method on the stability of redox systems

The effectiveness of the carbonate method is somewhat dependent on the redox properties of the sample and can without doubt be further optimized. In welding fumes the Cr^{+6} determination is principally disturbed by the presence of $\text{Fe}^{+3}/\text{Fe}^{+2}$, which for the carbonate method can be described by the following redox equation:

Equilibrium conditions can be evaluated with the help of calculating for the appropriate electrochemical cell as follows:

Following Nernst's equation

$$\text{E}_1 = \text{E}_1^0 + \frac{0.0591}{3} \log \frac{[\text{CrO}_4^{--}]}{[\text{Cr}(\text{OH})_3] [\text{OH}^-]^5} \quad (\text{m})$$

and

$$\text{E}_2 = \text{E}_2^0 + 0.0591 \log \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]}, \quad (\text{n})$$

such that

$$\text{E} = \text{E}_2 - \text{E}_1 = \text{E}_2^0 - \text{E}_1^0 + 0.0591 \log \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]} - 0.0197 \log \frac{[\text{CrO}_4^{--}]}{[\text{Cr}(\text{OH})_3] [\text{OH}^-]^5} \quad (\text{o})$$

where $\text{E}_1^0 = 0.13 \text{ V}$ and $\text{E}_2^0 = 0.770 \text{ V}$ are

Table 2. Results of chromium analyses of synthetic welding fumes of different chemical compositions with the carbonate method.

Sample no.	Composition					Results			
	MeCrO ₄		CrCl ₃ (mg Cr+3)	Fe ₃ O ₄		AAS		DPC	
	Me	mg Cr+6		mg	mg/mg Cr+6	Found (mg Cr)	Recovery (% Cr/ Cr+6)	Found (mg Cr+6)	Recovery (% Cr/ Cr+6)
22	Pb	9.7	0	0		9.4	97	9.9	102
23	Pb	8.2	0	0		7.7	94	—	—
24	Pb	71.0	0	0		75.8	107		
25	Pb	7.9	0	1,000	126.6	5.0	63	5.3	67
26	Pb	8.1	0	1,000	123.5	7.4	91		
27	Pb	70.3	0	5,000	71.1	68.8	98		
28	Pb	71.5	0	11,200	156.6	67.5	94		
29	Pb	9.1	49.7	0		8.1	89		
30	Pb	70.3	3.63	0		78.0	111		
31	Pb	9.2	41.3	1,000		5.9	64		
32	Pb	8.2	43.2	1,000		7.5	92		
33	Pb	69.1	4.06	5,000		68.2	99		
34	Ca	14.5	0	0		15.3	106		
35	Ca	14.0	0	1,000	71.4	12.0	86		
36	Zn	12.3	0	0		12.0	98		
37	Zn	48.2	0	0		51.8	108		
38	Zn	12.5	0	1,000	80	9.4	75		
39	Zn	49.6	0	5,000	100.8	38.7	78		
40	Zn	48.1	0	10,000	207.9	35.2	73		
41	Zn	12.5	58.8	0		12.5	100		
42	Zn	11.8	73.2	1,000		5.1	43		
43	Ag ₂	71.3	0	0		81.2	114		
44	Ag ₂	70.5	0	5,000	70.9	80.7	115		
45	Ag ₂	69.1	0	10,000	144.7	78.9	114		
46	K ₂	17.4	0	0		17.6	101		
47	K ₂	17.0	0	1,000	58.8	15.0	88		

the standard potentials for electrodes 1 and 2, respectively, according to Freier (8).

$$E = 0.640 + 0.0591 \log \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]} - 0.0197 \log \frac{[\text{CrO}_4^{--}]}{[\text{Cr}(\text{OH})_3]} + 0.0985 \log [\text{OH}^-] \quad (\text{p})$$

or

$$E = -0.739 + 0.0591 \log \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]} - 0.0197 \log \frac{[\text{CrO}_4^{--}]}{[\text{Cr}(\text{OH})_3]} + 0.0985 \text{ pH}. \quad (\text{q})$$

Under equilibrium $E = 0$ equation q can be rewritten as

$$\log \frac{[\text{CrO}_4^{--}]}{[\text{Cr}(\text{OH})_3]} = 5.00 \text{ pH} + 3.00 \log \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]} - 37.51. \quad (\text{r})$$

If the carbonate method is used with a welding fume matrix composed primarily of chromium and magnetite the concentrations $\text{Fe}^{+3}/\text{Fe}^{+2}$ will be determined by the pH of the solution as in fig. 1 and lead to:

$$\log \frac{[\text{CrO}_4^{--}]}{[\text{Cr}(\text{OH})_3]} = f(\text{pH}). \quad (\text{s})$$

This function $f(\text{pH})$ is sketched in fig. 4. It can be seen that a given concentration ratio $\text{Cr}^{+6}/\text{Cr}^{+3}$ will be in stable equilibrium at only one specific pH, which is then defined as optimal for the preparation of that sample. At a higher pH, the system will move towards a higher $\text{Cr}^{+6}/\text{Cr}^{+3}$ ratio and a tendency for the oxidation of Cr^{+3} to Cr^{+6} is implied. At a pH lower than optimum, the system will tend to move in the other direction, and Cr^{+6} will be converted to Cr^{+3} . The establishment of a stable equilibrium will depend somewhat on the reaction rate of the system,

which is a further function of temperature and concentration. Calculating the reaction rates for the system under consideration has proved to be extremely difficult. In general one can expect that Cr^{+3} reacts more slowly than Cr^{+6} and that Cr^{+3} , especially at a high pH, will be bound in basic polymeric compounds.

Alkaline fusion

Velocity constants have extremely high values during fusion, which should be ac-

Fig. 4. Relative distribution of Cr^{+6} and Cr^{+3} with thermodynamic equilibrium as a function of pH in a synthetic welding fume matrix.

Table 3. Results of chromium analyses with carbonate fusion.

Sample no.	Composition			Results	
	PbCrO (mg Cr^{+6})	CrCl_3 (mg Cr^{+3})	Fe_3O_4 (mg)	Found (mg Cr)	Recovery (% Cr/Cr^{+6})
48	11.8			12.0	102
49	6.85		1,000	6.25	91
50	7.63	33.72	1,000	21.33	280
51	9.53	35.01	1,000	34.44	360

companied by enhanced changes in the oxidation state (fig. 4). Thus with a sodium carbonate fusion of synthetic welding fumes, one should see a significant oxidation of the chromium which is present in low oxidation states. During sodium hydroxide fusion, oxidation by atmospheric oxygen can take place. Such reactions are represented in equation d. In order to demonstrate the theoretical oxidation effect, a series of synthetic welding fumes containing lead chromate and various amounts of chromic chloride and magnetite were analyzed with the carbonate fusion technique, and the results are presented in table 3. The high recovery rates (over 300 %) verify the significance of the effect in this system.

pH dependence of results of the carbonate method

The influence of pH on Cr^{+6} analysis in autoredox processes was studied in a series of synthetic welding fumes of known composition similar to that examined pre-

viously, through the systematic addition of acid to the carbonate leaching solution.

When the carbonate method was used with samples containing pure chromate, 100 % of the Cr^{+6} was recovered provided the pH was maintained at a level greater than 8, while only 80 % of the Cr^{+6} was recovered when magnetite was added at the same range of pH. This reduction in Cr^{+6} recovery was probably a result of adhesion to the hydrated iron compounds in the precipitate, in which case the effect can be eliminated by their removal. In agreement with the previous measurements, it was found that Cr^{+3} is not oxidized during analysis by the carbonate method at a high pH, a result in disagreement with the theoretical expectations (fig. 4), most probably due to the low reaction rate constant at the relatively low temperatures used in the analysis. The carbonate method was found not to be applicable at a low pH, as the amount of Cr^{+6} detected was either too high or too low, depending on the sample composition. Cr^{+3} was also dissolved and interfered, while chromates of low solubility were not dissolved because of the low carbonate concentration (due to evaporation of carbon dioxide). The ratio of the detected chromium concentration to the original Cr^{+6} content of the samples (Cr/Cr^{+6}), as a function of pH, for the sequence of synthetic welding fume compositions studied is shown in fig. 5, and a complete list of the analytical results is presented in table 4 (all for single determinations).

Fig. 5. Chromate recovery with the carbonate method as a function of pH for various matrices.

EXAMPLES OF APPLICATION OF THE CARBONATE METHOD

Stainless steel welding fumes

The carbonate method was used for the routine determination of total Cr^{+6} in welding fumes. The reliability of the method was verified by the analysis of actual samples of welding fumes to which known amounts of Cr^{+6} were added; chromium recovery in all of these cases was greater than 85 %, independent of chromium type, while the use of the DPC

method yielded a chromium recovery of between 27 and 85 %, depending on the type of welding process. Samples consisted of Millipore cellulose filters exposed in actual work situations; one-half of each filter was used for the determination of water-soluble and total hexavalent chromium, and the other half for the analysis of total elemental composition. Furthermore, total Cr^{+6} , water-soluble Cr^{+6} and chromium in other oxidation states was measured in samples of "reference standard" welding fumes of different compositions, produced in a welding robot used for the generation of fumes under well-defined and reproducible conditions. We observed that the total Cr^{+6} content of fumes appears to diminish with time, but, contrary to the assumptions of Abell (1), this is not primarily due to the filter itself, but is limited only to the water-soluble Cr^{+6} fraction and is mainly caused by the autoredox action of the fume matrix (Fe^{++}).

Water-soluble Cr^{+6} was measured by both the DPC technique and the carbonate

method; all chromium in the water phase was found to be Cr^{+6} . The amount and distribution of chromium (among oxidation states and fractions of different solubility) was found to be extremely dependent on values of the welding parameters. A detailed analysis of the chromium and total chemical content of welding fumes produced by different processes has been published (22, 23), and a study of the details of the parametric dependence of chromium in metal inert-gas (MIG) welding is under preparation (24). The general findings can be summarized by the comparison of the amount of chromium and the distribution among various oxidation states and solubilities for two common processes which represent the extremes of the physical situations encountered in welding technology involving stainless steel: manual metal arc (MMA) welding using coated electrodes and MIG. These results are shown in table 5 for stainless steel (SS) having a nominal composition of 18 % chromium and 8 % nickel; the total chromium content of fumes from mild steel welding is less than

Table 4. Results of chromium analyses of synthetic welding fumes of different pHs with the carbonate method.

Sample no.	Composition			Preparation pH	Results	
	PbCrO_4 (mg Cr^{+6})	CrCl_3 (mg Cr^{+3})	Fe_2O_3 (mg)		Found (mg Cr)	Recovery (% Cr/ Cr^{+6})
52	9.9	49.7	1,000	5	50.0	504
53	9.3	0	1,000	5	0.3	4
54	8.0	0	0	5	0.7	8
55	8.2	52.8	1,000	7.5	6.8	83
56	10.2	0	1,000	7.5	7.0	68
57	8.2	0	0	7.5	7.8	86
58	8.6	49.5	1,000	8.5	7.2	83
59	9.1	0	1,000	8.5	6.5	71
60	8.5	0	0	8.5	8.5	99
61	8.5	49.5	1,000	9.5	6.8	80
62	9.0	0	1,000	9.5	6.6	73
63	8.4	0	0	9.5	8.0	95
64	10.3	63.2	1,000	10.0	7.9	77
65	7.9	0	1,000	10.0	5.3	67
66	8.5	0	0	10.0	8.2	97
67	9.5	47.0	0	10.0	9.8	103
68	0	47.2	0	10.0	0.8	2
69	0	49.3	1,000	10.0	0.8	2
70	8.0	48.2	1,000	12	7.6	92
71	8.1	0	1,000	12	7.4	91
72	8.2	0	0	12	7.7	93

Table 5. Relative content and distribution of chromium (Cr) in stainless steel welding fumes.

Type of welding	Water-soluble (%)	Insoluble (%)	Total (%)
Manual metal arc (MMA)			
Cr ⁺³ + Cr	0	0.2 — 2.1	0.2 — 2.1
Cr ⁺⁶	2.2 — 4.3	< 0.03 — 0.42	2.2 — 4.3
Total Cr	2.2 — 4.3	0.2 — 2.5	2.4 — 6.4
Metal inert gas (MIG) argon, argon + 1 % oxygen			
Cr ⁺³ + Cr	0	3.56 — 13.78	3.56 — 13.78
Cr ⁺⁶	0.005 — 0.18	0.01 — 0.14	0.02 — 0.32
Total Cr	0.005 — 0.18	3.6 — 13.8	4.06 — 13.80

Fig. 6. Fractional analysis of welding fumes.

0.05 % for the MMA and 0.005 % for the MIG method.

Of the chromium occurring in fumes from MMA/SS processes, 5—33 % appears as either metallic chromium or Cr⁺³, which are totally insoluble in water, while 67—95 % is in the form of Cr⁺⁶, of which between 0—13 % is insoluble in water. For MIG/SS processes (with argon or argon with 1 % oxygen), 98.00—99.86 % of the chromium present is in the form of Cr⁺³ or metallic chro-

mium, which is completely insoluble, while 0.14—2.00 % appears as Cr⁺⁶, of which 60—90 % is insoluble in water.

Methods for determining the chemical composition of welding fumes including hexavalent chromium content and fractionation into elements according to solubility

The toxicity of many of the elements which can possibly appear in welding fumes (lead, chromium, nickel, tungsten, zinc, barium) is greatly dependent on the chemical compounds in which these elements occur. The permitted hygienic exposure levels (TVL's) for the individual compounds are frequently given in terms of both the relative solubility of the substances and the oxidation state of the elements. The evaluation of the burden placed on the welder by exposure to the fumes from various welding processes must therefore be based on a detailed analysis of the chemical composition of the fumes together with a determination of the elemental oxidation state and relative solubility. Hygienic samples frequently provide only limited amounts of material to work with (typically 1—5 mg) and therefore place additional demands on the analysis technique and make any standard fractionation process subject to significant errors.

Synthetic welding fumes consisting of Fe₃O₄ (57 %), PbCrO₄ (2.34 %), K₂Cr₂O₇ (2.33 %), Cr₂O₃ (11.73 %), NiO (11.67 %), NiCl₂·6H₂O (2.48 %), and MnO₂ (11.73 %),

corresponding to a typical distribution of elements and solubilities, were analyzed for chemical composition and solubilities by means of a procedure which is schematically shown in fig. 6. This procedure is considered to be optimal in terms of contamination and other problems and to have the minimum possible number of manipulations consistent with the recirculation of compounds through the preparation apparatus.

The specific steps of the procedure are as follows:

1. The weighed sample (or filter with known sample) is transferred to a 100-ml beaker, 25.0 ml of ion exchanged water is added, and the sample agitated at room temperature for 30 min. The resulting solution, together with the suspended matter, and the filter (if present) is transferred to a vacuum filter fitted with a 0.4 membrane filter. The filtrate (F_1) is separated for further analysis, and the remainder (R_1), including the 0.4 membrane filter, is returned to the original beaker.

2. To the beaker containing R_1 is now added 25.0 ml of a 7 % sodium carbonate solution, which is then raised to the boiling point and set aside to cool. The contents of the beaker are now filtered as in step 1, the filtrate F_2 separated for further analysis, and the remainder (R_2) returned to the original beaker (including all filters).

3. Filters and precipitates R_2 are now dissolved by boiling in nitric/hydrochloric acid and evaporated to dryness, and after sufficient cooling the residue dissolved in 25.0 ml of ion exchanged water. Any residue at this point (not dissolved by additional warming) is filtered once more, filters and residue forming R_3 , which is retained for further analysis, as is filtrate F_3 .

4. Residue R_3 is dried and ashed by incineration with hydrofluoric acid, or acidic or basic or, if necessary, oxidizing fusion. The sample is then filtered, if necessary, yielding F_4 for further analysis. In general R_3 is soluble in acid, whereby the water-soluble fractions F_3 and R_3 are eliminated.

5. Water-soluble chromium as found in welding fumes consists entirely of Cr^{+6} ;

therefore the AAS analysis of total chromium in F_1 can be considered sufficient to determine the water-soluble Cr^{+6} content of this material. In the case of uncertainty, however, F_1 can be analyzed specifically for Cr^{+6} by means of the DPC method or upon the addition of solid sodium carbonate to all or part of F_1 , whereby, after boiling, cooling and filtration, the resulting F_5 is analyzed for Cr^{+6} .

6. F_1 , F_2 , F_3 , F_4 , and F_5 are thereafter analyzed for the desired elemental content by means of AAS.

Liquid loss during boiling (steps 2 and 3), together with insufficient rinsing of the various filters, will probably represent the most significant sources of error, or a mixing of the different fractions.

Analysis of a long series of synthetic welding fumes shows that, with the single exception of nickel chloride ($NiCl_2$) (aqueous), the initial components are recovered in the proper fractions within the expected error limits (10 %); the low $NiCl_2$ recovery (69 %) is probably due a different hydration than expected.

The chromic acid used proved to be insoluble in acid and could first be dissolved by oxidizing alkali fusion. Since actual welding fumes are normally acid-soluble, it can be concluded that Cr^{+3} appears either as a hydrated sesquioxide or as picotite ($FeO-Cr_2O_3$). The latter is most probably the case since X-ray diffraction analysis of welding fumes containing chromium show only the magnetite structure (Fe_3O_4) (which is identical to picotite in crystal structure) with a possible line shift in the direction expected for increasing chromium content.

The results from synthetic welding fume analysis are presented in table 6. Fumes from actual welding processes, produced under well-defined conditions in a welding robot, were also analyzed according to the described technique; the results are assembled in table 7. It should be noted that the relative distribution of chromium among oxidation states and solubility fractions is extremely dependent on the values of the welding parameters (current, voltage, shielding gas, arc length) as indicated.

In contrast to the previous results (table 5 — where measurements have been made

Table 6. Elemental distribution of synthetic welding fumes^a in a fractional analysis.
(Continued on the next page)

Fraction ^b	Chromium (mg)			Lead (mg)			Potassium (mg)		
	Found	Ex-pected	% Re-covery	Found	Ex-pected	% Re-covery	Found	Ex-pected	% Re-covery
F ₁ (water soluble)									
A	0.30	0.33	91	0.003	0	—	0.285	0.326	87
B	0.049	0.038	129	0.003	0	—	0.039	0.038	103
F ₂ (sodium carbonate soluble)									
A	0.166	0.198	84	0.21	0	—	0.088	0	—
B	0.023	0.023	100	0.04	0	—	0.040	0	—
F ₃ (acid soluble)									
A	0.079	0—4.23	(2)	0.645	0.79	82	0.034	0	—
B	0.000	0—0.50	(2)	0.05	0.093	54	0.021	0	—
F ₄									
A	4.07	0—4.23	(96)	—	—	—	—	—	—
B	0.46	0—0.50	(92)	—	—	—	—	—	—
Total (F ₁ + F ₂ + F ₃ + F ₄)									
A	4.62	4.76	97	0.86	0.79	109	0.407	0.326	125
B	0.54	0.56	96	0.09	0.093	97	0.10	0.038	263

^a Synthetic welding fumes: Fe₃O₄ (57.7 %), PbCrO₄ (2.34 %), K₂Cr₂O₇ (2.33 %), Cr₂O₃ (11.73 %), NiO (11.67 %), NiCl₂ · 6 H₂O (2.48 %), MnO₂ (11.73 %).

^b A: 52.73 mg, B: 6.21 mg.

Table 7. Elemental distribution of welding fumes from stainless steel in a fractional analysis.
(Continued on the next page)

Sample	Welding parameters ^a			Chromium (%)				Nickel (%)			
				Water soluble	Sodium car-bonate soluble	Acid soluble	Total	Water soluble	Sodium car-bonate soluble	Acid soluble	Total
	Amp	Volt	mm	(F ₁)	(F ₂)	(F ₃)	(F)	(F ₁)	(F ₂)	(F ₃)	(F)
MO 17 ^b	170	16.5	1.8	0.31	0.096	4.70	5.11	0.151	0.024	4.49	4.67
MO 18 ^b	170	16.5	1.8	0.38	0.120	3.82	4.32	0.173	0.021	4.57	4.76
MO 19 ^c	110	16.8	2.8	0.24	0.083	4.93	5.25	0.109	0.026	3.11	3.25
MO 20 ^b	240	16.0	0.9	0.40	0.098	3.56	4.06	0.159	0.022	4.83	5.01
MO 21 ^d	250	26.5	2.5—3.8	0.17	0.113	4.96	5.24	0.089	0.021	4.53	4.64
MO 22 ^d	250	26.3	7.5—8.8	0.07	0.091	5.08	5.24	0.044	0	2.72	2.76
MO 23 ^d	285	26.3	1.9—2.5	0.11	0.087	4.18	4.38	0.067	0.010	4.39	4.47
MO 24 ^d	235	25.5	4.4—5.0	0.03	0.045	7.55	7.63	0.025	0.005	2.77	2.80

^a Electrode: 3RS17 1.6 mm ϕ (argon + 1 % oxygen).

^b Short arc transfer.

^c Drop transfer.

^d Spray transfer.

without the fractionation technique), an analysis of table 7 shows a lower total chromium content and, especially for short arc welding, an increased amount of water-soluble Cr⁺⁶. The data of table 7 are based on a larger diameter wire (1.6 mm) of the same type as used in table 5 (1.2 mm), and this variation may also account for some of the differences found. The analysis also unexpectedly showed that the fumes contain carbonate-soluble manganese and nickel compounds and that the manganese content and its distribution among the solubility fractions is extremely parameter

dependent. The distribution of nickel and manganese among the various solubility fractions has not previously been investigated for these fume types.

Additional uses of the carbonate method³

The applicability of the carbonate method for the analysis of Cr⁺⁶ in biological mate-

³ For an example of an industrial application of a similar method see Bombach and Luft (6).

Table 6. (continued)

Fraction ^b	Nickel (mg)			Manganese (mg)			Iron (mg)		
	Found	Ex- pected	% Re- covery	Found	Ex- pected	% Re- covery	Found	Ex- pected	% Re- covery
F ₁ (water soluble)									
A	0.222	0.32	69	0.0068	0	—	< 0.0005	0	—
B	0.026	0.038	68	0.018	0	—	< 0.0005	0	—
F ₂ (sodium carbonate soluble)									
A	0.035	0	—	0.013	0	—	0.011	0	—
B	0.013	0	—	0.0073	0	—	0.016	0	—
F ₃ (acid soluble)									
A	4.45	4.83	92	4.00	3.91	102	20.4	22.0	93
B	0.52	0.57	91	0.47	0.46	102	2.85	2.59	110
F ₄									
A	—	—	—	—	—	—	—	—	—
B	—	—	—	—	—	—	—	—	—
Total (F ₁ + F ₂ + F ₃ + F ₄)									
A	4.71	5.15	91	4.02	3.91	103	20.4	22.0	93
B	0.56	0.61	92	0.48	0.46	104	2.9	2.59	110

a Synthetic welding fumes: Fe₃O₄ (57.7 %), PbCrO₄ (2.34 %), K₂Cr₂O₇ (2.33 %), Cr₂O₃ (11.73 %), NiO (11.67 %), NiCl₂ · 6 H₂O (2.48 %), MnO₂ (11.73 %).

b A: 52.73 mg, B: 6.21 mg.

Table 7. (continued)

Sample	Welding parameters ^a			Manganese (%)				Iron (%)			
				Water soluble	Sodium car- bonate soluble	Acid soluble	Total	Water soluble	Sodium car- bonate soluble	Acid soluble	Total
	Amp	Volt	mm	(F ₁)	(F ₂)	(F ₃)	(F)	(F ₁)	(F ₂)	(F ₃)	(F)
MO 17 ^b	170	16.5	1.8	0.25	0.149	11.8	12.2	0	0.05	37.0	37.1
MO 18 ^b	170	16.5	1.8	0.31	0.151	9.1	9.6	0	0.06	35.9	36.0
MO 19 ^c	110	16.8	2.8	0.42	0.557	15.3	16.3	0.02	0.09	29.3	29.4
MO 20 ^b	240	16.0	0.9	0.24	0.299	9.5	10.0	0.01	0.08	35.5	35.6
MO 21 ^d	250	26.5	2.5—3.8	0.18	0.115	9.2	9.5	0	0.05	37.1	37.2
MO 22 ^d	250	26.3	7.5—8.8	0.27	0.105	15.1	15.5	0.01	0.02	34.9	34.9
MO 23 ^d	285	26.3	1.9—2.5	0.23	0.135	9.0	9.4	0	0.05	34.5	34.6
MO 24 ^d	235	25.5	4.4—5.0	0.22	0.076	12.7	13.0	0	0.03	35.8	35.8

a Electrode: 3RS17 1.6 mm^ø (argon + 1 % oxygen).

b Short arc transfer.

c Drop transfer.

d Spray transfer.

rial was studied in a series of preliminary measurements. Towards this end, a sample was synthesized by the mixing of 19 mg of Cr⁺⁶ (as potassium dichromate) with 5 ml of horse serum; 86 % of the initial Cr⁺⁶ was recovered with the carbonate method (compared to 101 % in the absence of the serum).

For comparison, Blomquist (5) found that only 2.5 % of the initial Cr⁺⁶ was recovered when the DPC method was used to analyze a sample consisting of 15 µg serum albumin and 4 µg Cr⁺⁶. Thus, in numerous

analytical situations with a need for the measurement of the distribution of chromium among the various oxidation states, the carbonate method would appear to be a practical solution, requiring only slight modification depending on the specific type of analysis required. The method has in fact been used for industrial hygiene measurements in the tanning and timber impregnation industries, which provide for other types of complex, organic matrices, as well as for process control and process development, e.g., control of the organic fixation of wood preservatives (Cr⁺⁶ to

Cr⁺³) and the indirect control of Cr⁺³ content of galvanizing baths.

SUMMARY AND CONCLUSIONS

Because of increasing concern for the health of workers, especially with respect to dermatitis and allergy-inducing substances active even in trace amounts, there is a specific need for reliable and sensitive analytical methods for the determination of the composition of industrial atmospheres. One specific need is for a method for the detection of Cr⁺⁶ compounds in fractions with different water solubilities, the demands of which appear not to be met by any previously used methods.

The carbonate leaching method described in this report represents a simple technique for the routine determination of total Cr⁺⁶ in complex matrices, of which welding fumes is a practical example. When used with synthetic welding fumes of known composition, more than 80 % of the original, slightly soluble and insoluble chromate can be recovered (in contrast to the DPC method for which recovery can be as low as 1 %). The remaining 20 % of Cr⁺⁶ can eventually be recovered through the addition of an extra wash step so that any Cr⁺⁶ adsorbed in the remaining precipitates can be liberated. The recovery rate achieved is, in any case, satisfactory for hygienic measurements (where other more significant errors can occur), so that the uncomplicated technique can be retained without modification for such application.

It is postulated that for each sample composition, determined by the presence of autoredox systems and the distribution of chromium among various oxidation states, there is a single well-defined pH for which the system will be in thermodynamic equilibrium. Preparation at a lower pH should be accompanied by a reduction of some unknown fraction of the Cr⁺⁶ initially present, while preparation at a higher pH could lead to the oxidation of chromium in lower oxidation states. Both situations were investigated with the use of synthetic welding fumes, and the expected change in oxidation state when the carbonate method was used at

a high pH was not found to take place, most probably due to the low reaction rate constant at the low temperatures (below 100°C) used. Thus the carbonate method can be used to determine the total Cr⁺⁶ content of welding fumes, a type of matrix for which other wet chemical methods have been shown to be unsuitable.

Pilot studies using this method on these aerosols indicate that the nature of the metallic compounds actually occurring in welding fumes varies greatly as a function of the welding method and welding parameter, and the possibility of a similar variation of biological activities for these substances is therefore implied. Extended studies to determine the exact nature of such effects are currently underway.

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