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AN ANALYTICAL PROCEDURE FOR DETERMINING CHROMIUM IN SAMPLES OF AIRBORNE DUST

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Abstract—A method is described for assessing occupational exposures to chromium aerosols; it involves four procedures. The first, proton induced X-ray emission (PIXE), measures the total chromium. The second, electron spectroscopy for chemical analysis (ESCA), measures the oxidation state of the particle surfaces, and the third, which uses sym-diphenylcarbazide (DPC), measures the proportion of water-soluble chromium VI. The fourth, transmission electron microscopy (TEM), provides information about the size and shape of the particles and guides the interpretation of the ESCA-data.

The multielemental nature of PIXE-analysis is advantageous in eliminating the possibility of interference in the DPC-method and in eliminating chromium compounds from the tentative list of existing health hazards in the smoke. These methods were applied to the analysis of samples of fume produced in welding, and information was obtained for the amounts of soluble and insoluble chromium (III and VI) in samples of different aerosols.

INTRODUCTION

EXPOSURE to chromium compounds constitutes a health hazard to workers in a number of different occupations. Ulcerations, dermatitis and respiratory cancers have been reported and the damage seems to depend on the oxidation state of the chromium and on the solubility of the particular compound involved, e.g., certain less water-soluble chromium (VI) compounds may be carcinogenic (NATIONAL INSTITUTE OF OCCUPATIONAL SAFETY AND HEALTH (NIOSH), 1975; HUNTER, 1976; HEALTH AND SAFETY EXECUTIVE (HSE), 1977; AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL HYGIENISTS (ACGIH), 1977). Hence in analysing the chromium contents of particles in work environments and for assessing the harmful effects of chromium exposure, it is useful to have an analytical tool capable of giving accurate information about oxidation states and solubility.

The common methods used for chromium analysis are atomic absorption spectroscopy (AAS) and colorimetry with sym-diphenylcarbazide (DPC). A variant of the DPC method (ABELL and CARLBERG, 1974) is recommended by NIOSH (1975). With these methods, although the total amount of chromium and the soluble chromium (VI) may be determined, no information is provided about the oxidation states of the insoluble chromium fractions. The procedure for analysing samples of airborne particulates reported here is capable of separating the different oxidation states of chromium and also soluble from less soluble chromium. The results of an investigation of samples of particles generated in welding operations in stainless steel are included.

METHODS

Particles are sampled on membrane filters and analysed with proton induced X-ray emission (PIXE), electron spectroscopy for chemical analysis (ESCA) and transmission electron microscopy (TEM) before and after washing in buffered water. After washing, the particles are considered to roughly resemble particles deposited in the lungs.

Elemental analysis

PIXE is a fast, reliable method for multielemental analysis with low detection limits (0.1–10 ng in routine analysis). For elements lighter than sulphur it is not quantitative. There are, however, a number of complementary methods which are capable of detecting several of these elements when used simultaneously with PIXE analysis. A review of the PIXE method has been published recently (Johansson and Johansson, 1976).

PIXE may be replaced by X-ray fluorescence (XRF) with only minor disadvantages, such as increased sample size and increased time of analysis. Atomic absorption spectroscopy (AAS) may also be used for the elemental analysis, but the capability of multielemental analysis is abandoned.

Oxidation state

The oxidation state of the chromium on the surfaces of the particles is studied by ESCA (Siegbahn *et al.*, 1967). The sample is bombarded with monoenergetic X-rays which induce outer electrons to leave atoms; the energies of these electrons yield information about the oxidation states on the surface. We have used aluminium K X-rays for excitation and an electrostatic electron spectrometer (AEI ES 200) for analysis of the energies of the ejected $2p_{3/2}$ electrons. For this study, standards with different ratios of Cr(VI)/Cr (total) have been prepared and analysed, giving an absolute accuracy of 0.1 and a detection limit of about 0.2 for the ratio Cr(VI)/Cr(total). Both the accuracy and the detection limit could be improved by using equipment capable of higher resolution. Because electrons ejected from the interior of the sample interact with other electrons on their way out, only a thin surface layer (about 2 nm) can be analysed. For very small particles and for particles consisting of aggregates of small identical particles the surface concentration is representative of the entire volume. For particles with diameters $<0.01\ \mu m$ ESCA is valid for more than 80% of the particle volume assuming spherical symmetry, whereas for particles with diameters $<1\ \mu m$, ESCA is valid for less than 1% of the volume.

Size and density

The transmission electron microscope is a versatile tool for studying the properties of individual welding fume particles (Frismark *et al.*, in press). From TEM information it is possible to estimate the representativeness of the ESCA data from the sizes of the particles and their density variations. The electron microscope used in this study was a Philips EM 300; an accelerating voltage of 100 kV gave a suitable transmission of electrons through the welding smoke samples used.

Solubility

The microenvironment encountered by particles deposited in the lungs is not fully understood. In this work a crude washing procedure, using a buffered water solution (NH_4NO_3/NH_4OH) at a pH of a bout 7.4 was employed. In the Tables below the 'soluble' mass of an element denotes the mass leached out of the particles with the washing procedure used and dissolved in the buffered solution. The concentration of water soluble chromium (VI) is analysed by the DPC method, in which sym-diphenylcarbazide forms complexes with water soluble chromium (VI), inducing a red-violet colour (SANDELL, 1959). The absorbance is measured with a spectrophotometer. The accuracy of this method is in the order of 5% for concentrations of Cr(VI) higher than 0.05 μg/ml. Allowance may have to be made for interference. In this investigation we have used a Perkin Elmer spectrophotometer and the absorbance was measured at a wavelength of 540 nm.

Filters

For evaluation of health effects, the respirable fractions of the airborne particulates are of special interest. Cyclone samplers (Casella personal samplers) have been used to collect the respirable fraction according to the Johannesburg convention (ORENSTEIN, 1959) on membrane filters. The cyclones require a flow rate of 1.9 l./min, which is too high for small pore size filters, which are necessary for surface deposition. The particles which penetrate into the filter are not seen by ESCA or TEM analysis.

For most applications a pore diameter of 0.025 μm is recommended. To simulate particle capturing in the nose and the upper respirable tract, an impactor stage with a 50% cut-off diameter of about 5 μm may be used instead of a cyclone.

If only the total filter-sample area were considered, one filter would be sufficient for the analysis suggested. However, the washing procedure is more conveniently applied to a whole filter than to a piece of a filter, thus it is feasible to use two parallel filters. In this investigation, samples have been collected on four filters (A, B, C and D) for each aerosol. Filters A and B—for PIXE analysis and ESCA—were membrane filters of mixed cellulose esters, of 0.8 μm pore diameter and of 37 mm diameter (Millipore AAWP 03700), allowing cyclone prestages to be used. The filter efficiency for the welding aerosol is estimated from SPURNY and LODGE (1972) to be almost 100% at a flow rate of 1.9 l./min. There is a minimum in the efficiency curve at about 0.7 μm diameter, but, even at the minimum, the efficiency exceeds 95%. The decrease of the PIXE sensitivity due to penetration into the filter is insignificant for the elements concerned in this work. For ESCA, a fraction of particles in the range of 0.7 μm diameter is lost into the filter. However, the welding particles are composed of aggregates of smaller spherical particles of uniform size, thus the Cr(VI)/Cr(III) ratio is not expected to be altered by this loss. When necessary, the uncertainty due to filter penetration should be avoided by applying 0.025 μm pore-size filter and an impactor stage.

Filters A and B are employed in parallel and are weighed before and after the sampling to check their comparability. Filter B is washed in the buffered solution. Each filter is then divided into two pieces—one for PIXE (pieces A1 and B1) and one for ESCA (pieces A2 and B2).

The thickness of the loadings of filters A and B is limited by charged-particle energy loss and by X-ray absorption in the PIXE analysis and should be less than 1 mg/cm^2 for the quantitative analysis of elements as light as sulphur. The lower limit to the thickness is determined by the decreasing accuracy in gravimetric determinations. For welding fumes a thickness of 50–100 μg/cm^2 is sufficient.

Filters C and D for the TEM analysis are also employed in parallel. A thin layer of carbon is evaporated on these filters before exposure. After exposure, filter D is washed and a second layer is evaporated on both filters C and D. The filter material is dissolved and a piece of the carbon–carbon sandwich is attached to a grid for TEM analysis of the particles. In this investigation 25 mm diameter filters of mixed cellulose esters with a pore diameter of 25 nm (Millipore VSWP 02500) have been used and they were dissolved in ethyl acetate.

The results of the PIXE analyses of pieces A1 and B1 give the total mass and the less soluble fraction respectively of all elements heavier than phosphorus. This information is relevant to the health hazard assessment; it is also used to evaluate possible interferences occurring in the ESCA and DPC analyses and to derive upper limits to the amounts of certain chromium compounds. The ESCA data from filters A2 and B2 give the ratios between Cr(VI) and total chromium on the surface of the unwashed and washed particles respectively.

WELDING FUME

Welding on stainless steel often produces high concentrations of chromium in the breathing zone. The fumes generated in welding with three different kinds of coated electrodes (a basic electrode, B; a high yield rutile electrode, R; a rutile-basic electrode, RB), all having a diameter of 3.25 mm, have been studied with the routine described above. The welding was performed on stainless steel containing 18% chromium and 8% nickel.

Fumes were collected in the laboratory arrangement (Akselsson *et al.*, 1977) shown schematically in Fig. 1. The fume is slowly sucked up through the column by the fan. Via a probe, which sweeps over the column section in a spiral path, the fume is sucked isokinetically to the two parallel filters.

For this feasibility test, five samplings were performed per electrode. The ratio between the masses of the loadings of the paired filters A and B was about unity. (The mean of 15 samplings was 1.02 and the standard error of the mean was 0.02.)

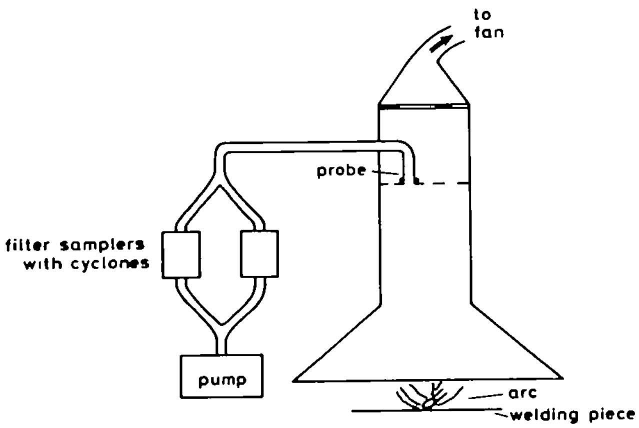

Fig. 1. The sampling arrangement designed by Malmqvist *et al.* (Akselsson *et al.*, 1977).

RESULTS

Table 1 lists the PIXE results for the fumes from the three electrodes. Chromium constitutes 2.5–5% of the total mass and about 70–90% of the chromium is readily soluble.

The analyses of the washing waters with the DPC method show the percentages of soluble Cr(VI) to be 1.7 ± 0.1, 1.5 ± 0.4 and 3.2 ± 0.3 of the total mass of the samples from electrodes R, RB and B, respectively. The uncertainties given are the limits of the 95% confidence interval.

Figure 2 shows ESCA spectra of an unwashed and a washed sample from the rutile high yield electrode. It is evident that there is Cr(VI) and Cr(III) on the particle surfaces before as well as after washing and that after washing the ratio between Cr(VI) and Cr(total) had decreased. Quantification of the ratios between chromium (VI) and chromium (total) has been estimated after calibration with a set of standards with the ratios 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0, prepared by mixing Cr_2O_3 and $K_2Cr_2O_7$. For the rutile electrode, ESCA data show 55–65% Cr(VI) before washing and 20–30% after washing. For electrodes B and RB, ESCA data show 90–100% Cr(VI) before washing. After washing, the concentrations of Cr(VI) and Cr(III) were too low to be detected by ESCA.

Table 2 summarizes the results. A large fraction of the chromium has been dissolved in the washing process, and in the residues after washing a large fraction is chromium III. Only the rutile electrode contains insoluble chromium VI. In this case, the detection limits prohibit ranking of the electrodes according to their chromium content of the fume. Figure 3(a) shows typical particles as seen in transmission electron microscopy. A low density material, probably derived mainly from the electrode coating, surrounds a high density core material, and acts as a glue holding aggregates of particles together. The shell has a thickness of about 0.03 μm; the material under it is not available for ESCA for reasons which have already been discussed.

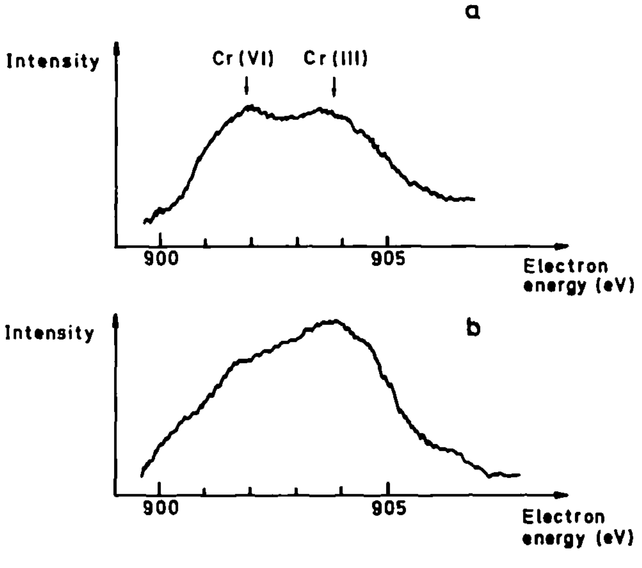

FIG. 2. ESCA spectra of (a) an unwashed and (b) a washed sample from a rutile electrode.

Table 1. Element concentrations in the fume from the three different electrodes found by PIXE analysis. The accuracy is about 10%, *n* is the number of observations

Element	Concentration in per cent and limits of the 95% confidence interval					
	Electrode R (*n* = 5)		Electrode RB (*n* = 5)		Electrode B (*n* = 5)	
	unwashed	washed	unwashed	washed	unwashed	washed
Cl	<0.2	<0.2	0.8 ± 0.4	0.6 ± 0.4	0.5 ± 0.2	0.15 ± 0.02
K	21 ± 1	2.8 ± 0.5	23 ± 2	<0.3	24 ± 5	0.71 ± 0.07
Ca	1.2 ± 0.1	0.19 ± 0.02	4.5 ±0.6	0.8 ± 0.3	12 ± 2	3.1 ± 0.5
Ti	2.1 ± 0.2	1.6 ± 0.2	1.5 ± 0.2	1.1 ± 0.5	0.6 ± 0.1	0.5 ± 0.1
V	0.05 ± 0.01	<0.02	<0.1	<0.05	<0.05	<0.02
Cr	3.4 ± 0.2	0.94 ± 0.12	2.9 ± 0.3	0.7 ± 0.3	4.0 ± 0.7	0.34 ± 0.06
Mn	2.7 ± 0.1	1.6 ± 0.2	15 ± 1	12 ± 5	3.0 ± 0.6	2.1 ± 0.3
Fe	3.3 ± 0.2	2.6 ± 0.3	2.8 ± 0.3	2.6 ± 0.8	4.3 ± 0.8	4.0 ± 0.5
Ni	0.22 ± 0.02	0.17 ± 0.03	0.38 ± 0.04	0.29 ± 0.06	0.31 ± 0.08	0.28 ± 0.05
Zn	0.33 ± 0.06	0.18 ± 0.04	0.18 ± 0.05	0.16 ± 0.06	0.25 ± 0.04	0.17 ± 0.03

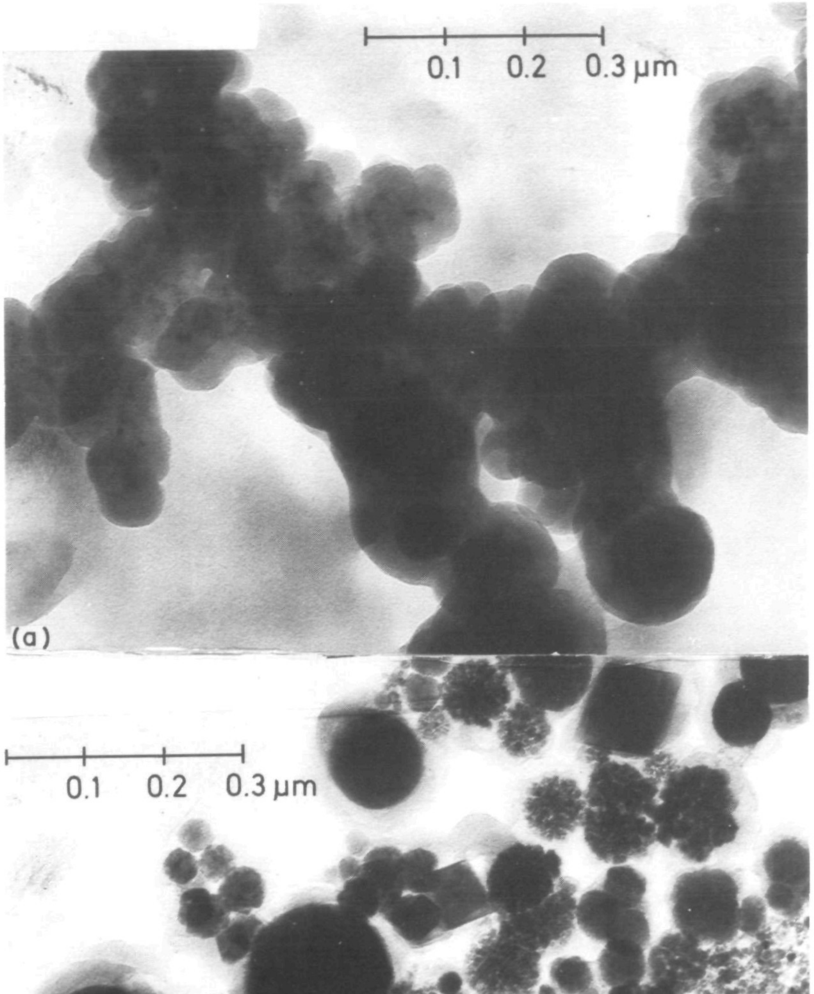

FIG. 3. Welding fume particulates as obtained by transmission electron microscope. Part (a) shows an unwashed sample and part (b) a washed sample. Notice the shell in (a) and the structure of the cores in (b); also the different appearance of the conglomerates in the two figures.

Table 2. Summary of information about chromium in welding particles found in this investigation. 'Insoluble' and 'soluble' mean undissolved and dissolved respectively in the washing procedure described in text

Method	Fraction	Percentage of chromium and limits of the 95% confidence interval		
		electrode R	electrode RB	electrode B
1 PIXE	total Cr	3.4 ± 0.2	2.9 ±0.3	4.4 ± 0.3
2 PIXE	insol Cr	0.94 ± 0.12	0.67 ± 0.25	0.34 ± 0.06
3 (1)–(2)*	sol Cr	2.5 ± 0.2	2.2 ± 0.4	4.0 ± 0.3
4 DPC	sol Cr(VI)	1.7 ± 0.1	1.5 ± 0.4	3.2 ±0.3
5 (3)–(4)*	sol Cr(III)	0.71 ± 0.25	0.69 ± 0.53	0.80 ± 0.4
6 ESCA†	insol Cr(VI)	0.25 ± 0.03	<0.2	<0.3‡
7 (2)–(6)†	insol Cr(III)	0.69 ± 0.12	0.67 ± 0.25	<0.3‡

* The difference between the analytical values mentioned.

† Assuming the Cr(VI)/Cr (total) ratios from ESCA to be representative for the samples.

‡ The chromium concentration is too low after washing to be detected by ESCA.

After washing [see Fig. 3(b)], a large part of the low density material is dissolved and information about the core material is obtained. Often the core is found to consist of an aggregate of small round particles of diameter about 0.01 μm. ESCA data are representative of about 80% of the particles of this size.

Associated errors

Some chromium VI may be reduced by the filter material and or by other constituents of the fumes (NIOSH, 1975). Acid environments facilitate the reduction. In ESCA, only the outermost nanometers of the sample are analysed and, because the thickness of the sample is normally of the order of 1 μm, the degree of reduction associated with the filter medium is not significant. To test how the Cr(VI)/Cr (total) ratio depends on the time between sampling and ESCA treatment, samples from electrode R fumes have been analysed 3 h to 5 months after sampling. One of the samples was stored under vacuum for 4 h and exposed to air less than 3 min before analysis. No significant (< 10%) change in the chromium ratio due to storage was found, suggesting that reduction between sampling and analysis performed within hours or even days is negligible.

There have been reports of reduction due to heating and/or X-rays from ESCA (De Angelis, 1976). For the fumes from the electrodes B and RB reduction can be neglected; almost 100% has been shown to be Cr(VI) before washing and neither Cr(III) or Cr(VI) were detected by ESCA after washing.

Figure 4 shows how the ESCA results for electrode R depend on the irradiation time. This time is defined as the time between onset of the irradiation and detection of the peak intensity of the Cr(VI) $2p_{3/2}$ electrons. The reduction effect is clear but not significant for health hazard assessment purposes. However, the ESCA-analyser used is not equipped either with a monochromator for the exciting Al K X-rays or with a modern focusing analyser. By using an ESCA-apparatus including these devices, a much less intense Al K X-ray beam could be used, which would eliminate the reduction effect almost completely.

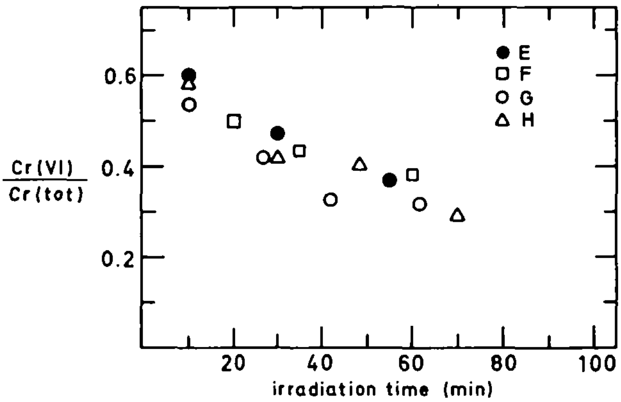

Fig. 4. The ratio Cr(VI)/Cr (total) from ESCA as a function of the irradiation time for particles generated in welding with electrode R. The samples E–H are identical but for sample E 4 h 45 min elapsed between sampling and the start of irradiation, for sample F 3 h 40 min elapsed, for sample G 35 days elapsed and for sample H 35 days elapsed. Sample H was cooled to −50°C during the irradiation whereas samples E–G were cooled to +25°C.

In the current work, the uncertainty due to reduction in the prepared standards is less than 10%.

Washing

The use of buffered solutions of pH 7.4 minimizes the risk of reduction or oxidation during washing. This pH value is also presumed to resemble that encountered by particles in the lung. In the washing procedure 25 ml of the buffered water was slowly filtered through the filter giving a washing time of 4–5 min per sample. By repeating the washing procedure in fresh buffered water, no more Cr(VI) could be washed out (less than 0.1 % of the mass of the fume). Thus, this procedure separates the readily soluble chromium from the less soluble.

If insoluble chromium passes through the filter during washing in particulate form, other insoluble elements are expected to follow in the same proportions. However, from Table 1 it can be seen that, e.g., 80–100% of the iron stays on the filter. Another test was performed by letting the washing water pass very slowly through a filter of pore diameter 0.4 μm. This filter was analysed by PIXE. Virtually no chromium (0.05% of the original chromium in the sample) was found on this filter. For electrode R the washing water was sucked through a filter having a pore diameter of 25 nm, and the chromium caught in this was less than 0.003% of the original chromium. This shows that particles do not pass through the filter in the washing process.

Interferences in colorimetry and ESCA analysis

A multielemental method such as PIXE is very useful in estimating the effects of interference in the colorimetric and ESCA techniques used. The major interfering ions in the DPC method for Cr(VI) analysis are Mo(VI), Hg(II), Fe(III) and V(V) (Sandell, 1959). The PIXE results shown in Table 1 indicate that molybdenum and mercury are absent (less than 0.2 %) in both the washed and unwashed welding samples, but that small amounts of vanadium (about 0.05%) are present in the latter. Interference from these small amounts of vanadium is negligible because good results may be obtained provided the ratio of vanadium to chromium (VI) is less than 10:1 (SANDELL, 1959).

In a sulphuric acid solution with chlorine absent, the yellow colour developed by iron is not strong and fairly good results are obtained when the transmittance of the solution is measured above a wavelength of 460 nm (SANDELL, 1959). In this experiment, because the absorbance was measured at 540 nm immediately after the addition of the reagent and because the chlorine concentration was less than 1 % according to the results of the PIXE analyses, the interference from iron is assumed to be negligible.

CONCLUSIONS

A procedure is described for the determination of chromium of different solubilities and different oxidation states for monitoring airborne particulates in work environments. The routine is feasible for samples consisting of very small particles. For larger particles, information abou surface·concentrations can be obtained and the surface concentrations may be most relevant for health hazard assessments. However, for homogeneous particles, extrapolations to bulk concentrations from the ESCA-data may not be reliable. As further information about the absorption mechanisms of chromium in the lungs becomes available, the washing procedure should be appropriately adjusted.

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