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Quantitation of Vanadium Oxides in Airborne Dusts by X-ray Diffraction

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Sampling and analytical methods employing membrane filter collection and X-ray diffraction analysis for vanadium pentaoxide (V_2O_5), vanadium trioxide (V_2O_3), and ammonium metavanadate (NH_4VO_3) in air are described. The analytical characteristics of five diffraction lines for V_2O_5, six lines for V_2O_3, and two lines for NH_4VO_3 were examined. The effect of particle size on instrument sensitivity was determined for V_2O_5 and V_2O_3. An aerosol generation system was built to provide replicate simulated field samples. The methods were evaluated by using both spiked and generated samples. The V_2O_5 method provides an overall precision (s_r) of 8.3% and a bias of 10.1% for the analytical range 170–2300 μg of V_2O_5 per sample. The V_2O_3 method provides an overall precision of 14.7% with a bias of −10.11%, over the range 64.5–625 μg of V_2O_3 per sample. Ammonium metavanadate can be determined with an overall precision of 26.3% and bias of −10.3%, over the range 21–225 μg of NH_4VO_3 per sample.

A number of vanadium-containing minerals are found in vanadium ores in the United States (*1*). These minerals are processed via salt roasting and acid leaching into vanadium pentaoxide (V_2O_5) and vanadium trioxide (V_2O_3). A third compound, ammonium metavanadate (NH_4VO_3) is an important commercial chemical made from the pentaoxide. Although not commonly found in mine dusts, the three compounds are produced in ore processing and may be present in the atmospheres of these operations. These materials have been implicated in a number of reports of respiratory illness in workers involved with processing operations (*2–6*). Determination and quantitation of the toxicologically significant compound requires a speciative rather than an elemental analytical method. This paper describes analytical methods for the three compounds as sampled by respirable-dust sampling devices (*7*).

Vanadium analysis has been the subject of many papers (*8*). Methods specific to particular vanadium compounds are, however, rare or they are not suitable for analysis of respirable-dust filter samples. Although X-ray diffraction is not generally considered a trace level analytical method, it was the most appropriate technique for chemical speciation for this type of sample.

Analytical methods based on the X-ray diffraction method for toxicologically significant chemicals in air have been developed at NIOSH for lead sulfide, quartz, zirconium oxide, zinc oxide, zinc oxide fume, titanium boride, and boron carbide (*9*). A successful sampling and analytical methodology has evolved from this work. This methodology, which is used in the present work, employs sampling with a 10-mm nylon cyclone and 37-mm 5-μm pore size PVC-type filter, dissolution of the filter with tetrahydrofuran, redeposition onto 25 mm diameter, 0.45-μm pore size silver filters, followed by X-ray diffraction analysis using external standardization. Redeposition redistributes the analyte as a homogeneous deposit on the silver filter and also permits a straightforward correction algorithm for X-ray absorption, based on the reduction of intensity of the d = 2.359 Å silver diffraction line (*10*).

Because the compounds are toxicologically active in the respiratory tract (*11*), sampling is performed with a 10-mm nylon cyclone which removes nonrespirable particles (*12*). This has the additional advantage of removing particles which reduce analytical accuracy due to absorption and extinction effects (*13*).

EXPERIMENTAL SECTION

Stock NH_4VO_3, V_2O_5, and V_2O_3 from Alfa Chemicals were tested for purity with inductively coupled plasma atomic emission (ICP-AES) analysis (as V, converted to the oxide): V_2O_5, 98.0%; V_2O_3, 99.9%; NH_4VO_3, 102.2%. Qualitative X-ray diffraction analysis of the compounds did not reveal unexpected diffraction lines, nor was interconversion of the oxides observed in fresh stock. V_2O_5 was found to be stable with time, as expected. The chemical stabilities of V_2O_3 and NH_4VO_3 are discussed separately below.

X-ray diffraction analysis was performed on a Philips APD Model 3500 instrument with 1° receiving slits, graphite monochromator, and Cu Kα radiation (λ = 1.54184 Å) (*14*). Intensity data were computed as the area of the diffraction line intensity vs. 2θ peak measured between a predetermined minimum and maximum 2θ; background correction was automatically computed from the intensities measured at those two points (*15*). The positions (2θ) of the two points, one on each side of the diffraction line, were obtained from a slow scan of the diffraction line under operating conditions (i.e., the same instrumental and sample characteristics as used for quantitation). The algorithm for converting raw diffraction intensities to air concentration of the analyte included a correction for the absorption of the X-rays by the matrix (see Appendix) (*16*).

Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed with a Jarrel-Ash AtomComp ICP-AE spectrometer (Model 1140) according to published procedures (*17*).

Usable X-ray diffraction lines were sought for each of the three compounds. Besides having appropriate intensity, the lines should be free from interference from the other two compounds, from silver or silver chloride found on the filter surface, and from quartz (which is ubiquitous in mine dusts). Several usable lines were investigated for each compound, although generally one line was clearly the most useful for quantitative analysis.

Sample Workup. Each sampler unit consisted of two PVC-type filters (type FWSB, MSA Corp., Pittsburgh, PA) in a closed-faced two- or three-piece cassette. For analysis, each cassette was opened and the filters were removed and placed in a 50-mL conical test tube. The filter was dissolved by the addition of 5 mL of tetrahydrofuran (THF) and placed in an ultrasonic bath for 10 min. The sample was quantitatively transferred to a filtration assembly containing a 25-mm diameter, 0.45-μm pore size silver filter (Selas Flotronics, Huntington Valley, PA) and rinsed twice with 5 additional mL of THF. A low vacuum was applied (<20 in. Hg) to redeposit the sample onto the silver filter. The sample was secured into a Philips XRD sample holder with Canadian Balsam cement and analyzed by X-ray diffraction.

Calibration of the Diffractometer. Standards for XRD analysis of the three oxides were prepared by spiking silver filters (0.45-μm pore size, 25-mm diameter) with known amounts of analyte. Each analyte was freezer-milled (−196 °C) for 10 min and sieved to <10 μm diameter so that the particle size approximated respirable sizes (*18*). Controlled weight of the analyte was determined by delivering predetermined volumes of a suspension of analyte (V_2O_5 in tetrahydrofuran, the others in 2-

Table I. Statistical Analysis of the Effect of Increasing Amounts of Mine Dust[a]

analyte	analyte load, µg	treatment (mine dust, µg)	analytical line (2θ)	significance of treatment (5% conf level)	av accuracy, %
NH_4VO_3	57	283, 578, 1130	15.04	no	17.8
		283, 578, 1130	18.10		14.6
	115	283, 578, 1130	15.04		8.3
		283, 578, 1130	18.10		22.4
	245	283, 578, 1130	15.04		−5.2
		283, 578, 1130	18.10		0.5
	560	283, 578, 1130	15.04		−18.7
		283, 578, 1130	18.10		−1.0
V_2O_3	281	0, 267, 567, 1117	54.28		−10.5
		0, 267, 567, 1117	33.18		−10.2
		0, 267, 567, 1117	24.39		−24.2
V_2O_5	282	0, 259, 518, 776, 1035	20.27	yes	20.5
		0, 259, 518, 776, 1035	21.73	yes	12.2
		0, 259, 518, 776, 1035	31.05	no	−0.3

[a] Six samples at each treatment load level were analyzed.

propanol) by glass pipet or (for V_2O_3) by a suspension delivery system described below. Standards were made up as follows: V_2O_5, 63–2008 µg of V_2O_5 per filter in triplicate; V_2O_3, 98–294 µg of V_2O_3 per filter in quadruplicate; and ammonium metavanadate, 61–305 µg of NH_4VO_3 per filter in triplicate. Tetrahydrofuran was used for V_2O_5 because it did not dissolve V_2O_5 nor did it cause flocculation of the V_2O_5 or adhesion to the glass container surfaces.

Spiked Filters. *V_2O_5.* A suspension of sieved V_2O_5 in 500 mL of acetonitrile was made. While the suspension was being magnetically stirred, aliquots were withdrawn and pipetted onto two PVC filters mounted on a Millipore filtration apparatus (Millipore part no. XX10-047-00) at loadings of 233, 466, and 688 µg of V_2O_5 per filter (six at each level).

NH_4VO_3. As above, samples were spiked onto PVC filters at levels of 109, 164, and 277 µg of NH_4VO_3 per filter.

V_2O_3. Because of the higher density of V_2O_3 (4.87 g/cm^3), the pipet spiking technique described above occasionally gave poor results. As an alternate method of obtaining aliquots of V_2O_3 suspension, a suspension delivery system was built. The system contained a Talboys Model 102 impeller stirrer (Talboys Engineering Co., Emerson, NJ) to keep the suspension mixed without introducing bubbles and a Manostat peristaltic pump (Manostat Corp., New York, NY) to deliver the suspension at a constant flow rate. An electronic timer (Chrontrol Model CT, Linburg Enterprises, San Diego, CA) turned the peristaltic pump on for a specific number of seconds. The system was calibrated gravimetrically with 2-propanol. Volume control was precise to of <1% s_r. The masses of spiked analyte per filter using the apparatus were 107, 214, and 322 µg of V_2O_3.

Generated Samples. An eight-sample generation system described previously (*19*) was used to generate sets of samples loaded with V_2O_5. A cyclone on the fluidized bed limited the aerosol to particles in the respirable size range; cyclones were not used on the sample cassettes. Each generated set contained eight samples: six two-piece closed-face cassettes each containing double 37-mm PVC filters plus backup pad (two filters atop the pad), and two cassettes each containing a single 37-mm mixed cellulose ester filter (Millipore type AAWP) plus backup pad, as a control. All filters were handled carefully to prevent movement of the deposition. Controls were analyzed by ICP-AES for an independent determination of analyte aerosol concentration.

Vanadium trioxide and ammonium metavanadate were generated in a similar but larger 12-sample capacity generation system described elsewhere (*20*). As above, a cyclone on the fluidized bed restricted the aerosol to respirable-size particles. The air flow through the cassettes was maintained by 2-L/min calibrated critical orifices. For each generation of samples containing V_2O_3, ten cassettes with double PVC filters and two with single cellulose ester filters were used as controls. For NH_4VO_3 sampling, nine cassettes with double PVC filters and two with cellulose ester filters were used.

Mine Dust Matrix Studies. For each analyte, double PVC filters were spiked with specific amounts of mine dust and of analyte (both were freezer-milled for 10 min and sieved, <10 µm diameter). At a given loading level of analyte, a series of mine dust loadings were made. Six samples were loaded with each mine dust/analyte load level combination. These loading levels are given in Table I. Loading of mine dust was performed first. The double PVC filters were exchanged (i.e., the bottom filter was placed on top), then the analyte was loaded on. Both analyte and mine dusts were made up with weighed quantities of material suspended in 1 L of suspension liquid. For V_2O_5, the suspension liquid was acetonitrile; for the others, 2-propanol was used.

Analysis of the samples containing mine dust with V_2O_5 required slight alteration of the 2θ range (minima and maxima) where diffraction lines from the mine dust interfered with analyte lines. Calibration samples were reanalyzed where alteration was required. In these cases, changes in slopes of the calibration curves were slight.

RESULTS AND DISCUSSION

Vanadium Pentaoxide Analytical Method. Vanadium pentaoxide (V_2O_5) has five diffraction lines of potential analytical quality (20.27, 41.32, 21.73, 31.05, and 26.21 °2θ). In the course of investigating these lines for quantitative use, a significant variation of the relative intensities of the lines with different samples had been observed (*7*). This variation was apparently due to the dissimilar average particle size of the samples and was considered a particle size effect (probably due to preferred orientation (*21*) arising from the *c* axis cleavage plane of V_2O_5) (*22*). The effect strongly influenced the slope of the calibration curve and consequently must be considered in any quantitative X-ray diffraction analysis. A suitable means of avoiding the effect was to employ the 31.05 °2θ line for quantitative analysis. That line has been shown to exhibit a minimal change of intensity with particle size (*7*).

The method was tested with spiked and generated filter samples. Silver filters were spiked with V_2O_5 and were analyzed by X-ray diffraction using each analytical line and the data converted to mass of analyte using the calibration curves described above. Similarly, samples were generated in the eight-sample generation system described in the Experimental Section. The 41.32 °2θ line was found to be so weak as to preclude use for quantitative analysis; the 21.73 °2θ line was not used due to its proximity to the silica line at 20.85 °2θ. The 20.27 °2θ line was investigated, despite the silica interference, because of its high intensity. Analytical results are summarized in Table II for V_2O_5 and the other two analytes. For both spiked and generated samples, the 31.05 °2θ line provided the best accuracy and precision. Comparison of analytical results for spiked and generated samples indicated that sampling with PVC-type filters was highly efficient, and that losses due to the redeposition step were negligible.

Table II. Results of Vanadium Compound Analysis

		low			medium			high				
analyte	analyte line (2θ)	load, μg	precsn, % s_r	bias, %	load, μg	precsn, % s_r	bias, %	load, μg	precsn, % s_r	bias, %	pooled precision % s_r	av bias, %
					Spiked Sample Analysis							
V_2O_5	20.27	233	12.5	71.0	466	6.8	5.6	699	10.3	25.6	10.2	34.1
	26.21		18.2	46.2		9.2	13.5		4.9	−3.0	12.1	18.9
	31.05		6.3	34.3		6.3	6.9		4.0	7.7	5.7	16.3
V_2O_3	24.39	107	9.9	9.1	214	8.5	15.2	322	5.9	12.1	12.2	8.2
	33.18		13.6	27.7		5.2	26.3		6.6	21.0	25.0	9.2
	36.38		11.7	23.7		8.9	32.5		4.2	24.6	26.9	8.8
	54.29		25.0	−9.0		9.0	2.6		11.2	17.5	3.7	16.7
NH_4VO_3	15.07	109	13.0	31.1	164	7.3	15.8	277	5.9	3.6	9.3	16.8
	18.10		7.1	20.5		5.9	3.6		8.6	10.8	7.3	11.6
					Generated Sample Analysis							
V_2O_5	20.27	100.2	5.1	32.7	275.0	6.4	24.1	322.0	6.1	27.5	5.9	28.1
	26.21		9.5	−19.6		14.1	−23.6		3.8	−10.3	10.0	−17.8
	31.05		7.5	6.9		7.0	12.5		6.9	14.1	7.2	11.2
V_2O_3	24.39	64.5	17.4	3.7	323.0	10.9	−11.2	640.5	6.7	−20.0	13.4	−10.1
	33.18		20.2	−1.8		9.8	3.8		17.0	−10.9	14.7	0.0
	36.38		21.2	17.8		10.8	12.3				14.3	14.2
	54.29		29.2	1.7		17.6	−20.4		6.6	−11.7	18.9	−10.1
NH_4VO_3	15.07	23.8	28.1	−5.1	173.0	23.5	12.6	228.0	17.4	29.7	23.7	11.4
	18.10		23.7	−11.7		36.4	−17.2		10.3	0.0	25.8	−10.2
	21.46		56.5	10.3					15.8	15.6	41.5	13.2

During the course of this work, improper sealing of a PVC filter in the sampler cassette was occasionally observed if only one filter was used. In addition, some types of PVC filters tested (currently not in production) were tested and found to not filter the material effectively—particulate was observed on the backup pad. These difficulties were avoided by using two PVC filters in each cassette. This was done throughout this work.

On the basis of the MSHA exposure limit for vanadium dust (0.5 mg/m^3) (*1*), a sampling/analytical method should cover the analytical range of about 200–800 μg of V_2O_5 per sample. The samples generated in this series of experiments covered the range of 170–2300 μg per filter, so that the proposed range was exceeded. The method provided an overall precision (*23*) of 8.25%, with a bias of 10.1% (generated samples) for the analytical range 170–2300 μg of V_2O_5 per filter, which corresponds to 0.2 to 2.8 times the TLV (assuming a volume of 816 L). The time stability of the compound was estimated to be at least 1 year, based on repetitive analysis of the calibration curve spiked samples. The compound was quantitatively sampled by the filtration technique utilized; penetration was negligible. A summary of the characteristics of the various analytical lines for all three analytes is given in Table III.

Vanadium Trioxide Analytical Method. Qualitative X-ray diffraction analysis of V_2O_3 on various types of filters revealed lines of potential analytical quality at 24.39, 33.18, 36.38, 49.83, and 54.28 °2θ. Diffraction lines for vanadium pentaoxide and ammonium metavanadate do not interfere with those of V_2O_3.

Although V_2O_5 is chemically stable at ordinary laboratory and industrial environments, some disagreement exists as to the stability of V_2O_3, especially at higher temperatures and humidity (*12*), with respect to oxidation to V_2O_5. In order to determine the stability of the V_2O_3 as it pertains to sample storage, a series of loadings of V_2O_3 (freezer-milled and sieved to <10 μm diameter) on 0.45-μm silver filters was made in December of 1982, stored in a laboratory storage box at ambient temperature and humidity, and analyzed periodically for 15 months. No significant changes in the intensities of the 24.39, 33.18, or 49.83 °2θ lines were seen; apparently the compound was stable under these conditions. It was concluded that V_2O_3 samples can be stored under these conditions for several months without affecting analytical accuracy.

The effect of particle size on the corrected intensities of the V_2O_3 diffraction lines was investigated by experiments similar to those described above for V_2O_5 (*7*). These investigations showed that mass-corrected intensity did not change significantly with particle size for the 24.39, 36.38, 54.28, and 33.18 °2θ lines. This is consistent with the crystal morphology of V_2O_3, which unlike V_2O_5 does not have a strong cleavage plane (*26*).

As with V_2O_5, silver filters were spiked with V_2O_3 (107–321 μg per filter) and analyzed. At or below a loading of ~100 μg of analyte, the relative standard deviation (s_r) exceeded 10% for all analytical lines. Samples were also obtained from atmospheres of V_2O_3 at concentrations of 0.24 to 2.57 mg/m^3 (as V_2O_3). Of the potential analytical lines, the 24.39 °2θ and 54.28 °2θ lines were relatively intense and free of interferences. Of these, the 24.39 °2θ line had superior precision. This line provided an overall s_r of 14.7%, with a bias of −10.1% over the air concentrations investigated. Adequate precision can be obtained, assuming a 4-h sampling time, for compliance testing at the permissible exposure limit promulgated by the Mine Safety and Health Administration of 0.5 mg/m^3 as V_2O_5. No problems with particle breakthrough or cassette leakage were observed when sampling with doubled PVC filters.

Ammonium Metavanadate Analytical Method. Potentially useful analytical lines for NH_4VO_3 were found at 15.07, 18.10, 21.46, 23.60, 28.21, 30.74, and 34.12 °2θ. The 65.25 °2θ line was not investigated because of proximity to a silver reflection at 64.48 °2θ. Two lines, at 41.42 and 49.83 °2θ, were not retained in subsequent experimentation due to low intensity. Of the remaining four lines, the 18.10 °2θ line was considered the most acceptable analytical line due to its intensity and freedom from previously encountered interfering lines from mine dust samples.

Although NH_4VO_3 is stable in ordinary environments, it decomposes at ~200 °C to V_2O_5, NH_3, and H_2O (*27*). The compound loaded on PVC filters was observed to turn yellow, apparently due to formation of V_2O_5, after a few days when

Table III. Characteristics of Analytical Lines for Vanadium Oxides

d space, Å	rel intens[a]	peak 2θ	scan		detection limit,[b] μg	calibration slope, ct/μg	precision,[c] % s_r	bias,[d] %	comments
			min 2θ	max 2θ					
Vanadium Pentaoxide									
4.38	100	20.27	19.4	20.9	4	205.0	11.5	−28.9	silica interference 20.85 °2θ
4.09	35	21.73	20.9	22.4	13	57.1			silican interference 20.85 °2θ
3.40	90	26.21	25.5	26.6	10	54.2	11.3	−22.3	silica interference 26.69 °2θ
2.88	65	31.05	30.3	31.4	9	73.0	8.3	10.1	good
2.185	17	41.32	40.5	41.6	28	24.9			weak; V_2O_3 interference 41.42 °2θ
Vanadium Trioxide									
3.65	60	24.39	24.75	23.5	6	75.1	14.7	−10.1	good
2.70	80	33.18	33.5	32.5	5	78.3	16.0	0.0	AgCl interference 32.32 °2θ
2.47	60	36.37	36.8	35.7	9	70.6	15.6	14.2	silica interference 36.53 °2θ
2.18	20	41.42	41.7	40.6	62	11.7			weak; V_2O_5 interference 41.32 °2θ
1.83	25	49.83	50.4	49.3	21	30.2			weak
1.69	100	54.28	54.5	53.3	5	91.2	20.7	−10.1	good
1.43	30	65.25[e]							
Ammonium Metavanadate									
5.88	50	15.07	14.3	15.4	7	133.8	24.0	11.4	good
4.90	75	18.10	17.7	18.2	7	101.4	26.3	−10.2	good
4.14	95	21.46	21.0	21.8	10	49.8		13.2	weak; V_2O_5 interf 21.73 °2θ
3.77	40	23.60	23.1	23.9	18	38.5			weak; V_2O_5 interference 41.32 °2θ
3.164	100	28.21[f]				50.3			AgCl interference 27.88 °2θ
2.912	60	30.74	30.1	30.9	21	33.9			weak
2.628	45	34.12	33.5	34.4	20	36.0			weak

[a] From ref 24 (λ = 1.541 84 Å). [b] Reference 25. [c] $s_r = \{GRSD^2 + 0.1667 \cdot SRSD^2 + 0.05^2\}^{1/2}$, where GRSD is the generated-sample pooled relative standard deviation and SRSD is the spiked-sample pooled relative standard deviation (ref 22). This is the estimated relative standard deviation for the total (sampling plus analytical) air-monitoring method. [d] From generated samples. [e] Not evaluated because of an Ag interference at 64.48 °2θ. [f] Not evaluated because of an AgCl interference at 27.88 °2θ.

exposed to an ordinary laboratory environment. In order to determine the stability of the NH_4VO_3 as it pertains to the sampling and analysis method, a series of loadings on various types of filters were made in May, 1984, stored in the open at room temperature and humidity, and analyzed routinely for several months. A significant decrease in the intensity of the 15.07 °2θ diffraction line of NH_4VO_3 was observed, probably due to conversion of NH_4VO_3 to V_2O_5 (Figure 1). On the basis of these data, it is important that analysis for NH_4VO_3 be made within 1–2 weeks of sampling. Some improvement is obtained by redeposition onto silver filters for storage. Storage in a freezer resulted in neglible decomposition and is recommended for sample storage. As is clear from Figure 1, concern for stability of NH_4VO_3 is especially critical for samples on PVC-type filters.

The effect of particle size on diffraction line corrected intensities as investigated for V_2O_3 and V_2O_5 could not be determined for NH_4VO_3 because of the rapid decomposition of the analyte into V_2O_5 during the classification of NH_4VO_3 dust into size fractions. The decomposition was apparently a result of the dispersion of the particles into the air and the corresponding large increase in the exposed surface area.

The method was evaluated with spiked NH_4VO_3 samples over the range of 109–277 μg per filter and with generated samples (using the 12-sample generation system as described in the Experimental Section) with atmospheres of 0.037–0.435 mg/m^3 of NH_4VO_3. The 15.07 and 18.10 °2θ lines were reasonably intense and approximately equal in performance. The 18.10 °2θ line is recommended because, at a higher 2θ, it does not require as much absorption correction. By use of that line, the method provided an overall s_r of 26.3%, with a bias of −10.2% over the generation range. Lack of correlation between calibration slopes and powder diffraction file relative intensities (Table III) indicates that preferred orientation effects may be occurring.

Mine Dust Matrix Studies. Prior to quantitative analysis, any field sample should be examined for the presence of interferences. A strongly interfering line may necessitate the use of a different diffraction line for quantitative analysis. A less severe interference may be avoided by redefinition of the 2θ limits used to define the analytical line, with concomitant restandardization. In order to estimate the effect of typical mine dust matrices as interferences in the analytical methods described above, a study was undertake in which the methods were applied to samples containing various amounts of multicomponent mine dust added to the pure analyte.

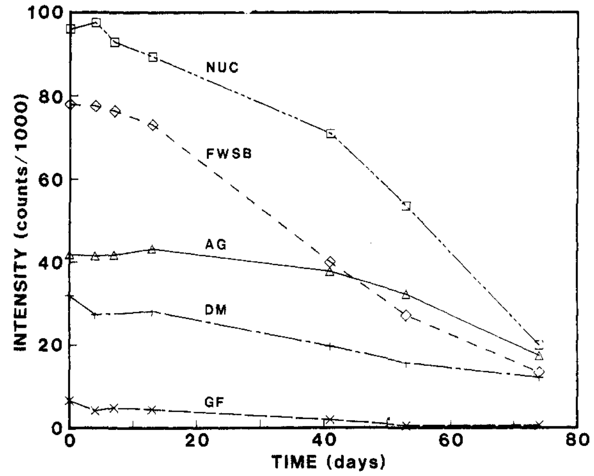

Figure 1. Stability of 301.1 μg of NH_4VO_3 deposited on various types of filters. Filter types are as follows: NUC, Nuclepore polycarbonate filter, 1-μm pore size; FWSB, MSA type FWSB PVC filter, 5-μm pore size; AG, Selas silver filter, 0.45-μm pore size; DM, Gelman DM450 PVC filter, 0.45-μm pore size; GF, Gelman type A/E glass fiber filter. The variation in intensity is a result of the absorption by the filter material and differences in filtration efficiency. No absorption correction was applied to the intensities.

Samples of 12 different ores from three uranium/vanadium mines near Uravan, CO, were crushed and freezer-milled and scanned qualitatively by XRD. In general, the 12 samples

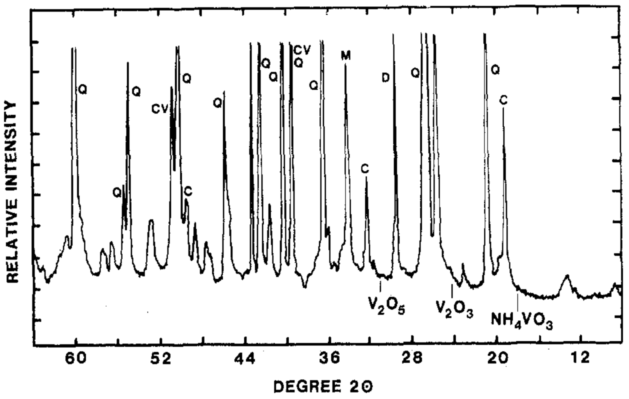

Figure 2. Diffraction pattern of a vanadium/uranium mine dust sample from the Deremo-Snyder Mine, Section 10, tailings blasted 12-6-82, ~2% uranium. Probable identifications of some diffraction lines are indicated: quartz (Q), corvusite (CV), dolomite (D), montroseite (M), and coffinite (C).

contained the same mineral species; however, the relative intensities of the diffraction lines differed considerably. One ore sample, designated sample 1 (Deremo-Snyder Mine, Section 10, tail blasted 12-6-82, ~2% uranium) and characterized by a large number of distinct lines, many of which were absent or reduced in the other samples, appeared to have the greatest potential for interference. This sample was reexamined in more detail (Figure 2). Quartz, corvusite, coffinite, and possibly montroseite and dolomite were identified. Several lines could not be assigned. Neither sample 1 or the other ore samples had significant interferences for the recommended analytical lines for the three analytes. Minor interferences with the 20.27, 21.73, and 31.05 °2θ lines of V_2O_5 were evaded by redefinition of the respective 2θ minima and maxima. No diffraction lines due to V_2O_5, V_2O_3, or NH_4VO_3 were observed in the pure mine dust from any of the 12 ores.

In order to approximate field samples in which unprocessed mine dust was present along with V_2O_5, V_2O_3, or NH_4VO_3, filters spiked with one of the analytes were additionally spiked with varying amounts of mine dust from sample 1 ore as described in the Experimental Section. The weights of analyte and mine dust employed are given in Table I. These were then analyzed for the analyte by X-ray diffraction. Analytical accuracy and precision for the sets of analyses are given in Table I. A calculation of the statistical effect of addition of mine dust (F-test) using a standard two-factorial statistical experimental design (*28*) indicated no significant effect (at a 95% confidence level) for any analytic line, except for the 20.27 and 21.37 °2θ lines of V_2O_5. The latter problem can be avoided by using the 31.05 °2θ line for quantitation.

The characteristics of the analytical methods and detection limits for the three compounds are listed in Table III (*29*). A limit of quantitation (LOQ) of about 100 μg per sample for each analyte was estimated from the work performed on the method development, assuming ideal conditions (no interferences) and using the recommended analytical lines of 31.05 °2θ (V_2O_5), 24.39 or 54.28 °2θ (V_2O_3), and 18.10 °2θ (NH_4VO_3). Other analytical lines may have a significantly higher LOQ. The recommended lines avoid common interferences (e.g., silica, Ag, AgCl) and particle size effects on diffraction line intensity. Due to reduced reflectivity, detection limits are not as low as those with strongly diffracting materials such as silica.

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APPENDIX

The following procedure was used for conversion of raw diffraction intensity into concentration of analyte, including correction of X-ray diffraction intensities for absorption of the X-rays by the sample and matrix (*15*).

The concentration of analyte, C, in the air sample is

$$C = \frac{([\hat{I}_x f(T)] - \hat{I}_b)}{mV} \text{ mg/m}^3$$

where

m = slope of calibration curve (counts/μg)

$$f(T) = \frac{-R \ln T}{1 - T^R} = \text{absorption correction factor}$$

$R = (\sin \theta_{Ag})/(\sin \theta_x)$,
where θ is the X-ray diffraction line angle

$T = \hat{I}_{Ag}/\hat{I}^{\circ}_{Ag}$ = transmittance of sample

V = actual air volume sampled at sampling site (L)

$\hat{I}_x$ = normalized intensity for sample peak

$\hat{I}_b$ = average normalized intensity for blank

The transmittance of the sample, T, is determined by the decrease in the intensity of the silver d = 2.359 Å line. It is computed from the net normalized intensity count of the silver peak on the sample filter, $\hat{I}_{Ag}$, and of the normalized intensity count of the six blank filters, $\hat{I}^{\circ}_{Ag}$. Scan times were 0.5 s/0.02 °2θ for the silver peak and 10 s/0.2 °2θ for the analyte peak. The silver peak was scanned from 37.03 to 39.03 °2θ.

Normalized intensites (denoted by a circumflex) are determined by measuring the net count, I_r, of a reference specimen (mica, Arkansas stone, or other stable standard) before each unknown, standard, or media blank is scanned. Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak. The normalized intensity for the analyte and silver peaks on each sample, media blank and standard are calculated as follows:

$$\hat{I}_x = (I_x/I_r)N$$

Registry No. V_2O_5, 1314-62-1; V_2O_3, 1314-34-7; NH_4VO_3, 7803-55-6.

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Optimization of Perchlorination Conditions for Some Representative Polychlorinated Biphenyls

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The yield of decachlorobiphenyl (DCB) from representative Aroclors (50 to 6000 ng) using antimony pentachloride as perchlorinating agent was extremely temperature dependent below 236 °C for a reaction period of 2 h. At 288 °C, a 35-min reaction period was sufficient to obtain DCB yields $>80\%$ for Aroclors 1016, 1242, 1254, and 1268. The perchlorination process was shown to be first order. The temperature dependence of the reaction times below 236 °C was largely responsible for the inconsistent perchlorination yields reported previously in the literature. The extraction of DCB with hexane from a HCl-acidified perchlorinated solution and the subsequent column chromatography on silica gel were also essential after the perchlorination to quantitate the DCB by ^{63}Ni electron capture/gas chromatography. The structures of the two nonachlorobiphenyls, which were the penultimate stable intermediates before DCB, were found. The methodology to use the technique for air and blood samples was described.

Polychlorinated biphenyls (PCBs) are ubiquitous in environmental and biological samples (*1–3*). PCBs are usually isolated through hexane extraction of an aqueous sample or after hydrolysis. The extract is then further fractionated by column chromatography and identification/quantification achieved by ^{63}Ni electron capture or Hall conductivity detector gas chromatography (ECD/GC and HC/GC, respectively). For quantifications, at least five major peaks of the original standard are utilized (*4*). However, interfering peaks often make identification and quantification difficult, necessitating more subfractionation. Furthermore, nonstandrd chromatograms may also occur as a result of differential biological metabolism of individual PCB isomers (*5*), differential solubilization of low chlorine-containing PCB isomers in water (*6*), and differential volatilization of the low-chlorine-containing isomers into air (*7*). In addition, industrial capacitors may contain mixtures of PCBs as could spills and hazardous wastes, rendering pattern recognition of complex gas chromatograms an uncertain tool to identify PCBs. Even the Webb-McCall method (*8*) basedon halogen conductivity detector results relies on knowing the PCB type before quantification. Because PCB quality may vary from lot to lot, the original determinations of chlorine content by Webb and McCall (*8*) may only be approximate. Gas chromatograpy/mass spectrometry (GC/MS) identification, though isomer specific, is extremely costly and is best suited for confirmation purposes when levels may be of biological or environmental interest; it is not a routine screening tool.

The major alterntive method is perchlorination (*9–15*) of PCBs to decachlorobiphenyl (DCB). Though isomer specificity is lost, enhanced sensitivity is attained since all PCB isomers are converted to DCB, and the ECD response to DCB is much greater than those for the PCB isomers observed most in samples (tetra-, penta-, and hexachlorinated). Samples have to be split to identify if biphenyl is present since the latter will yield DCB on perchlorination. However, quantitation of only DCB is certainly easier than of four to five isomers and DCB can be readily confirmed by GC/MS. Pattern recognition can then be applied (*3, 16, 17*) to the unperchlorinated sample. If the overall chlorine content can be estimated, the amount of original PCB can be qualitatively found. This is an inexpensive screening method compared with GC/MS analyses.

The key to such a screening method is the quantitative perchlorination of microamounts of PCBs. There are three current reagents: antimony pentachloride (*9–13, 18*), BMC reagent (*9, 10, 15*), and antimony pentachloride–iodine–sulfuryl chloride (*10*). These have been utilized to perchlorinate

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