CONFIRMATION OF VANADIUM PENTOXIDE IN WORKPLACE ATMOSPHERES

Method Number: ID-185

Matrix: Air

OSHA Permissible Exposure Limits
Final Rule Limits (as V_2O_5):
Respirable dust: 0.05 mg/m³ Time Weighted Average (TWA)
Fume: 0.05 mg/m³ (TWA)

Transitional Limits (as V_2O_5):
Total dust: 0.5 mg/m³ (Ceiling)
Fume: 0.1 mg/m³ (Ceiling)

Sampler: Low-ash polyvinyl chloride (PVC) membrane, 37-mm diameter, 5-µm pore size. The membrane is placed in a cassette which is then attached to a 10-mm nylon cyclone (optional for fume sampling) and a calibrated personal sampling pump.

Recommended Sampling Rate: 1.7 liter per minute (L/min)

Analytical Procedure: The PVC membrane is dissolved in tetrahydrofuran and a suspension is produced with the collected dust. The dust is transferred to a silver membrane for analysis by XRF and verification by XRD.

Recommended Air Volume: 816 liters (8-h sample)
For confirmation only

Quantitative Detection Limits: (as V_2O_5)

X-ray Diffraction		X-ray Fluorescence	
DL	Total time	DL	Total time
25 µg	65 s	14 µg	100 s
20 µg	650 s	2 µg	1,000 s

Precision and Accuracy
Validation Levels: 0.29, 0.58, and 0.87 mg/m³ (as V_2O_5) using 237, 474, and 710 µg V_2O_5 loadings and assuming 816 liter air volumes

Respirable Dust:	X-ray Fluorescence (See Section 3.2.)	
	Fine-Respirable	Respirable
CV_1	0.097	0.064
Mean Recovery	87.1%	96.5%
Overall Analytical Error	±32%	±16%

Method Classification: Validated Confirmation Method

Chemist: Mike C. Rose

Date: October, 1987 (revised April, 1991)

CONFIRMATION OF VANADIUM PENTOXIDE IN WORKPLACE ATMOSPHERES

Branch of Inorganic Methods Development
OSHA Technical Center
Salt Lake City, Utah

Note: OSHA no longer uses or supports this method (December 2019).

CONFIRMATION OF VANADIUM PENTOXIDE IN WORKPLACE ATMOSPHERES

1. Introduction

The goal of this method is to provide confirmation for occupational vanadium pentoxide (V_2O_5) exposures. To achieve that end, the published X-ray diffraction (XRD) approach presented in a NIOSH study (8.1.) for various V compounds was evaluated for applicability. Unlike the NIOSH study, this method focuses on only V_2O_5. The method was further extended to evaluate the applicability of X-ray fluorescence (XRF) to measure V_2O_5 exposures, since sample preparation was also compatible with XRF analysis.

The procedure used in the NIOSH XRD study was adapted from the published analytical procedure (8.1.) and techniques (8.2.) that were in print prior to the publication of NIOSH Method 7504 (8.3.). The NIOSH sampling approach collects and analyzes only the respirable fraction because of its toxic effects (8.1.). [Vanadium pentoxide is also toxic by other routes of exposure (8.4.-8.6.).]

Particle size effects on the analysis were investigated during the OSHA validation when the OSHA PEL was for total dust and fume (i.e. Transitional PELs). The respirable particle-size range was used for validation of this method because of the size dependence associated with XRD. The validation is applicable to the newer Final Rule V_2O_5 PELs because total dust is now excluded other than consideration as nuisance dust. The OSHA V_2O_5 PELs are currently for respirable dust or fume and are 8-h time weighted average (TWA) values (8.7.).

1.1. History

The previous two OSHA methods for V were atomic absorption spectroscopy (AAS) (8.8.) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) (8.9.). Both methods analyze for the element V and do not speciate the particular V compound present.

This method was validated in 1987 using a Finnigan direct-beam energy dispersive X-ray fluorescence (EDXRF) spectrometer and a Philips automated powder diffractometer (APD). More recently, field samples submitted to the Laboratory for V_2O_5 analyses have been analyzed using a Kevex EDXRF spectrometer that features substantially improved software and an Fe secondary target that reduces background and offers improved analytical performance. Detection limit and sensitivity data for both the direct-beam and secondary target instruments are included in this method. A more complete description of the X-ray instrumentation used in this method is given in reference 8.10.

1.2. Analytical Principles

1.2.1. XRD:

Quantitative powder XRD relies upon the diffraction of monochromatic X rays by the regular lattices of randomly oriented crystallites uniformly deposited in a thin flat film. The relationship among the parameters of order (n), X-ray wavelength (λ), the lattice spacing (d), and the angle of diffraction (Θ) is given by the Bragg equation:

$$n\lambda = 2d \sin \Theta$$

1.2.2. XRF:

Thin film quantitative X-ray fluorescence relies upon the excitation of atoms in a uniformly deposited thin flat film by the application of X rays of sufficient energy to cause the promotion of inner orbital electrons and subsequent decay accompanied by characteristic fluorescence.

1.2.3. XRD and XRF:

For uniform thin films, these X-ray techniques produce signal intensities that are proportional to the amount of analyte present. Non-linear calibration curves can also be used to correct for the fluorescing Ag support medium, shadowing of particles in Ag membrane pores, preferred orientation, and particle-size effects (8.10.).

1.3. Advantages and Disadvantages

1.3.1. Advantages of both methods:

Both methods are non-destructive. Further analyses may be performed on the sample by dissolution in acid and using atomic absorption (8.8.) or atomic emission (8.9.) methods.

1.3.2. Advantages of XRD:

The XRD method is specific for determining V_2O_5.
The sampling and analytical approach provides the opportunity for concomitant analysis for respirable quartz and/or zinc oxide by XRD (8.11. and 8.12.).

1.3.3. Advantages of XRF:

Energy dispersive XRF provides the opportunity for the serendipitous discovery of other toxic elements that might be present in the air sample. For example, Pb and U are present in many V ores (8.1., 8.4., 8.6.).

Detection limits may be significantly decreased for the XRF analysis by increasing the data collection time.

1.3.4. Disadvantages of both:

The XRF and XRD instrumentation are expensive.

1.3.5. Disadvantages of XRD:

Quantitation by XRD is particle-size dependent and the sample distribution should match that of the standard reference material. This necessitates using a 10-mm nylon cyclone with a personal pump operated at 1.7 L/min to collect all samples except for fume. The use of a cyclone will preclude certain particle-size ranges; therefore, if a cyclone is used, the dust collected will only be in the respirable range. For total dust samples where a cyclone is not used, the XRD method is used only as a confirmation technique.

The presence of a non-V_2O_5 interference in some blanks precludes significantly decreasing detection limits in the XRD method by increasing the data collecticn time.

Preferred-orientation effects are potentially large for XRD analyses of V_2O_5, due to cleavage along favorable planes (8.1.).

1.3.6. Disadvantages of XRF:

X-ray fluorescence (XRF) cannot speciate the vanadium-containing compound.

Positive interferences can occur from Ti or Cr (Also see Section 4.2.).

1.4. Vanadium Pentoxide (CAS 1314-62-1) Some Sources of Exposure (8.6.):

Application	Source of Exposure
catalyst	oxidation of nitrogen and sulfur oxides
colorant	manufacture of yellow glass
developer	photography industry
coating	using welding rods
alloys	manufacture of special steels
contaminant	cleaning fuel oil burners

1.5. Physical and Chemical Properties (8.5., 8.6.):

Molecular weight : 181.90
Specific gravity : 3.35
Melting point : 690 °C
Boiling point : 1750 °C (decomposes)
Vapor pressure : non-volatile at room temp.
Aqueous solubility : 0.8 g/100 mL at 20 °C

1.6. Toxicology

Information contained in this section is a synopsis of current knowledge of the physiological effects of V_2O_5 and is not intended as a basis for OSHA policy.

1.6.1. When inhaled, the chief effects of V_2O_5 are on the respiratory passages. Tracheitis, bronchitis, emphysema, pulmonary edema, or bronchial pneumonia may be observed, but no specific chronic lung lesions have been described. Other symptoms reported include eye irritation, conjunctivitis, dermatitis, green tongue, metallic taste, throat irritation, increased mucus, and cough (8.6.).

1.6.2. The toxic effects of V_2O_5 are primarily from exposures to dusts in the respirable particle-size range. Exposure to non-respirable dust can also produce toxic effects.

1.6.3. Death has been observed when animals were exposed to 70 mg/m^3 for a few hours (8.6.).

2. Range, Detection Limit, and Sensitivity (8.10.)

This method was evaluated when the OSHA PELs were Ceiling total dust and fume values. It should perform well under the more recent 8-h TWA respirable dust and fume OSHA PEL (8.7.).

2.1. Loadings of 237 to 710 µg V_2O_5 were evaluated. The calibration curves are usable up to at least 2,500 µg V_2O_5, the highest loading used in the method. Both X-ray methods require a thin layer deposition of sample; therefore sample loadings greater than 2,500 µg V_2O_5 should be split up on separate Ag membranes.

2.2. The quantitative detection limits (DL) for V_2O_5 depend upon the X-ray data collection time. The following detection limit estimates were obtained:

X-ray Diffraction		X-ray Fluorescence			
		Direct-Beam		Secondary Target	
DL	Total time	DL	Total time	DL	Total time
25 µg	65 s	14 µg	100 s	0.25 µg	100 s
20 µg	650 s	2 µg	1,000 s	0.10 µg	600 s

2.3. The sensitivity (S) expressed in counts/µg (as V_2O_5) is also dependent upon analytical time:

X-ray Diffraction		X-ray Fluorescence			
		Direct-Beam		Secondary Target	
S	Total time	S	Total time	S	Total time
18	65 s	4	100 s	120	100 s
180	650 s	40	1,000 s	720	600 s

3. Method Performance (8.10.)

3.1. X-ray Instrumentation

The XRF portion of the method was evaluated in 1987 using a direct-beam energy dispersive X-ray fluorescence (EDXRF) spectrometer and an automated powder diffractometer (APD). Advances in X-ray instruments should enable users to obtain similar or better results than that obtained in the method evaluation. Other X-ray targets and detectors may be used as appropriate. Some newer instrumentation combines X-ray diffraction and fluorescence features.

3.2. Dust Characterization

In order to assess the method performance as a function of particle size, both coarse and fine V_2O_5 respirable dust materials were investigated during the evaluation of this method. Both materials passed through a 10-µm sieve. The approximate particle-size distributions of the two materials were measured by optical microscopy. The approximate size-distributions found are as follows:

Material	0.5 to 3 µm	3 to 10 µm
Coarse	50%	50%
Fine	99%	1%

These results are approximate and are only used to show that the median visible particle size of the coarse material approximated the 3.5 µm median diameter that is characteristic of respirable dust (8.13.). This coarse material was referred to as "respirable dust" in the evaluation and was used to assess the method performance for respirable dust.

Particles below 0.5 µm could not be counted directly using optical microscopy. Visual observations of acetonitrile suspensions of the coarse and fine materials indicated that a significant amount of the fine material had a very small particle size; after thorough mixing, the suspension of the coarse material cleared over the course of a day whereas the suspension of the fine material remained cloudy for several days. The fine material consisted of particles of 3 µm or less and had a particle-size distribution strongly biased towards smaller particle sizes than respirable dust; however, it includes a particle size range that is also deposited in the lung. The size distribution of the fine material was comparable to that expected for samples collected with a cyclone. This material was referred to as "fine respirable" in the method and was used in preparing calibration curves, because the method of preparation was more reproducible than that for the coarse material.

The XRD recovery for coarse material prepared and analyzed on Ag membranes was twice that found for the fine material. The results for the fine-respirable and respirable dust samples are tabulated below:

Dust		X-ray Diffraction	X-ray Fluorescence
Respirable	CV_1 Range	0.0555 - 0.0830	0.0392 - 0.0795
Respirable	CV_1 Pooled	0.068*	0.064
Fine-respirable	CV_1 Range	0.0946 - 0.1663	0.0612 - 0.1456
Fine-respirable	CV_1 Pooled	0.121*	0.097
Respirable	Recovery Range	163.4 - 190.2%	95.7 - 97.6%
Respirable	Recovery Mean	177.4%*	96.5%
Fine-respirable	Recovery Range	85.9 - 91.1%	84.8 - 89.4%
Fine-respirable	Recovery Mean	88.7%*	87.1%
Respirable	Overall Error	± 91%	± 16%
Fine-respirable	Overall Error	± 36%	± 32%

* Average results from two APDs sharing the same generator.

These results indicate there are unacceptably severe errors associated with particle-size effects in the case of analysis of V_2O_5 by XRD. The XRF method is more immune to errors due to particle-size effects and is therefore potentially more accurate if the sample particle-size distributions cannot be reliably matched to the standard material. It should be emphasized that the XRF method only analyzes for V. Samples should normally be quantitated by XRF and qualitatively confirmed by XRD.

After the method validation, a secondary-target EDXRF spectrometer that offered improved analytical performance was obtained. A preliminary study using field samples submitted for V_2O_5 confirmation analysis has shown that results from samples prepared on Ag membranes and analyzed by the secondary-target XRF were in excellent agreement with results obtained using an ICP-AES method (8.9.). The Ag membrane samples were acid-digested after the XRF analysis and diluted solutions were analyzed for V using the ICP.

4. Interferences

4.1. XRD

For XRD, any crystalline material with a diffraction peak in the location of the XRD diffraction line at 31.05° 2θ is an interference. An earlier study (8.1.) indicated no interferences in common mineral compositions that contain V_2O_5. During the evaluation (8.10.), a significant low-level positive interference was observed in some of the blanks and was not attributable to V_2O_5.

4.2. XRF

Note: The potential interferences for XRF were assessed using a Link Systems EDX slide rule (Nashua Corp., Los Angeles, CA) to gauge other analyte signals and their proximity to the V K_α and V K_β peaks.

The V XRF lines have potential positive interferences. Known potential interferences are tabulated in Table 1. Depending on the resolution of the instrument and the available deconvolution software, the most significant likely interferences on an instrument with a resolution of 0.15 to 0.17 kV peak width at half height are the Ti K_β peak which overlap the V K_α peak and the Cr K_α peak that occur at the V K_β peak. Depending on the instrument geometry, Ag diffraction peaks from the Ag membrane are also possible. The Ti K_α peak may interfere with background correction.

Sum peaks occur when the counting rate is too high to accurately measure the energies of the X-ray photons and the energies of two or more photons are counted as a single photon. This error can be reduced by decreasing the X-ray tube current or through corrections using computer software. Samples containing large amounts of sulfur or chlorine may produce sum peaks at the V K_α and V K_β peaks, respectively. Because the sample is deposited on a Ag membrane, Ag sum peaks may interfere with the V K_β peak. The Ag sum peaks occur in the range of 5.266 to 7.038 kV with a maximum intensity located near 5.4 kV.

When present in large amounts, iron and cobalt could give Si escape peaks in the vicinity of the V K_α and K_β positions. An escape peak is generated by the low-probability quantum excitation of the K-shell electrons in the Si atoms of the detector producing a small peak at 1.76 kV below its parent peak.

Absorption edges (ab) are step discontinuities in the Energy vs. X-ray absorption function. The peak intensity reduction is greater if the absorption edge is on the low energy side of the V K_α peak. Absorption-edge effects are not expected to be significant for the thin films used in this method.

The remaining interferences are the L lines of other elements which, when present, tend to be of low intensity.

5. Sampling

5.1. Sampling Equipment

5.1.1. Sample assembly:

Filter holder consisting of a two- or three-piece cassette, 37-mm diameter.

Backup pad, 37-mm, cellulose.

Low ash PVC membrane filter, 37-mm, 5-µm pore size [part no. 625413, Mine Safety Appliances (MSA), Pittsburgh, PA or cat. no. P-503700, Omega Specialty Instrument Co., Chelmsford, MA].

Note: During preparation for analysis, the sample is dissolved in tetrahydrofuran (THF). Certain acrylic copolymers added to PVC filters are insoluble in THF. If the membrane filter composition is unknown, a laboratory test should be conducted with THF to determine suitability before use.

5.1.2. Cyclone: Nylon, 10-mm (BDX-99R, part no. 7010048-1 Sensidyne Inc., Largo, FL, or part no. 456243, MSA, Pittsburgh, PA).

Note: A cyclone is optional for fume sampling. If a mixture of fume and dust is anticipated, a cyclone should be used.

5.1.3. Pump calibration system: Stop watch and bubble tube or electronic meter.

5.1.4. Sampling pump: Calibrate the personal sampling pump to approximately 1.7 L/min. Use a representative sampler (cyclone, filter, etc.) in-line with the pump to minimize errors associated with uncertainties in the volume sampled. For fume sampling, the cyclone is optional and the pump can be calibrated at 2 L/min.

5.1.5. Assorted flexible tubing.

5.1.6. High volume sampling pump with cyclone (optional - for bulk sample collection). Whenever possible, take a high volume respirable V_2O_5 dust sample for laboratory use as a respirable dust reference material. This is beneficial because V_2O_5 has significant particle-size effects in XRD.

5.2. Sampling Procedure

5.2.1. Place the PVC filter and a cellulose backup pad in a two- or three-piece cassette.

5.2.2. Attach the cassette, which is preceded by a 10-mm nylon cyclone (optional for fume sampling), to a calibrated personal sampling pump using flexible tubing. Do not use tubing on the inlet port of the cassette.

5.2.3. Place the sampling assembly in the breathing zone of the worker or sampling area and place the pump in an appropriate position. Take 816 L of air through the cassette at approximately 1.7 L/min. Do not allow the cyclone to be inverted during or after sampling. **Take full shift samples if possible.** Collect fume samples without a cyclone at 2 L/min flow rates.

5.2.4. Check the pump and sampling assembly periodically to verify performance and to monitor particulate loading on the sample filter. If the filter becomes overloaded (>3 mg) during the sampling interval, replace it with another filter.

5.2.5. Terminate sampling at the predetermined time and record the pump flow rate and collection time.

5.2.6. Record on the OSHA 91 form all pertinent sample data. When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the samples. Request "confirmation analysis of vanadium pentoxide".

5.2.7. Identify and submit an appropriate blank filter from each lot of filters used.

5.2.8. Seal each filter cassette and identify it with an OSHA Form 21. Mail samples to the laboratory in a suitable container designed to prevent damage.

5.3. Wipe samples are not appropriate for this analysis, but may be submitted for analysis by ICP-AES.

5.4. Bulk samples are appropriate, especially if they represent settled dust.

5.5. Bulk samples should be shipped separately from air samples. They should be accompanied by Material Safety Data Sheets if available. A description of the sample composition is useful in resolving interferences and should accompany bulk samples. Check current shipping restrictions and ship to the laboratory by the appropriate method.

6. Analysis

Samples are analyzed by both XRD and XRF. Only one sample preparation method is necessary; both analytical techniques are compatible with this sample preparation.

6.1. Safety Precautions

6.1.1. Follow laboratory safety rules and regulations regarding solution preparation and instrument operation.

6.1.2. Refer to the appropriate manuals for proper instrument operation and maintenance. Analysts that are unfamiliar with the instrumentation must be trained prior to using the equipment. Refer all non-routine maintenance to an X-ray specialist or authorized service personnel. Wear a radiation badge and a radiation ring when using the X-ray equipment. Be sure any radiation monitors are operating properly.

6.1.3. Tetrahydrofuran (THF) is **extremely flammable** and tends to form **explosive peroxides.** If static electric discharge is a potential problem, use a grounded wrist strap when transferring THF. Fires involving THF are likely to rapidly become fierce; in case of a large fire, sound an alarm and evacuate.

6.1.4. Use appropriate caution when handling chemicals. Use latex or other chemically-resistant gloves to avoid skin contact with solutions and suspensions of THF and V_2O_5. Both chemicals are **toxic.** Tetrahydrofuran defats skin. Read the Material Safety Data Sheets. Use a hood for ventilation and use a fit-tested respirator if necessary when grinding or preparing samples. Dispose of any waste properly.

6.2. Equipment

Either a direct-beam or a secondary-target XRF instrument can be used. A wavelength-dispersive XRF instrument can be used in place of an EDXRF instrument.

6.2.1. Direct-beam XRF:

The spectrometer should be equipped with appropriate monitors and collimators. The spectrometer used at the OSHA Salt Lake Technical Center (OSHA-SLTC) included the following accessories:

a) Indium-lined collimators.
b) Polypropylene window film, 0.20 mil thick (part no. 3520, SPEX Industries, Edison, NJ).
c) Rhodium X-ray tube.
d) Laboratory press, 12 ton (Cat. no. A14-100, Kevex, San Carlos, CA.).
e) Lithium-drifted silicon (SiLi) detector.
f) Radiation safety monitor (S.E. International Instrumentation Model Radiation Alert Monitor 4, S.E. International Instrumentation Division, Summertown, TN). This safety monitor can be used with other X-ray equipment below.

6.2.2. Secondary-target XRF:

The spectrometer should be equipped with appropriate monitors, collimators, and secondary targets. In addition to the accessories listed in 6.2.1. items c-f, the secondary-target XRF spectrometer at the OSHA-SLTC included the following accessories:

a) Lucite monitor.
b) Tantalum collimator.
c) Iron secondary target.
d) Sample holders for 25-mm diameter Ag membranes (Cat. no. A00-213, Kevex). Note: These holders may require light machining in order to center the Ag membrane over the most sensitive spot.
e) Pellet die set for preparing multi-channel analyzer (MCA) energy calibration sample, 31-mm diameter (Cat. no. A10-403, Kevex). Alternately, a 13-mm diameter die set (Cat. no. A10-401, Kevex) may be used.
f) Sample holder for 31-mm diameter MCA energy calibration sample (Cat. no. A00-214, Kevex). Note: If a 13-mm diameter pellet is used, substitute a 13-mm diameter sample holder (Cat. no. A00-212, Kevex).

6.2.3. XRD system consisting of:

a) Automated Powder Diffractometer (APD).

b) X-ray Generator.
c) Long, fine-focus copper target X-ray tube.
d) Scintillation, position sensitive, or xenon proportional counter detector.
e) X-ray accessories include: pulse-height analyzer, graphite monochromator, 2θ compensating slit, 1° receiving slit, and sample spinner.
f) Sample holders for 25-mm diameter Ag membranes (Model no. PW1813/26, Philips Electronics Instruments Co., Mahwah, NJ).
g) Recirculating cooling system for the X-ray tube.

6.2.4. Computer system consisting of:

a) Hardware and software for data reduction and graphic presentations.
b) Line profile library (JCPDS-International Center for Diffraction Data Powder Diffraction File, JCPDS, Swarthmore, PA).

6.2.5. Standard and sample preparation:

a) Low ash PVC membrane filters, 37-mm, 5-µm pore size [part no. 625413, Mine Safety Appliances (MSA), Pittsburgh, PA or cat. no. P-503700, Omega Specialty Instrument Co., Chelmsford, MA].
b) Analytical balance capable of 10 µg precision.
c) Centrifuge tubes: Round bottom 40-mL (Pyrex 8260).
d) Gloves, THF-resistant [such as latex gloves (Cat. no. 8852, American Pharmaseal Lab., Glendale, CA)].
e) Volumetric pipettes, eyedropper, volumetric flasks and graduated cylinders.
f) Magnetic stirring bar and stirrer.
g) Forceps.
h) Silver membrane filters: 25-mm diameter, 0.45-µm pore size (Cat. no. FM25-0.45, Osmonics, Inc., Minnetonka, MN).
i) Ultrasonic bath.
j) Filtration apparatus: 25-mm (Filter Holder Hydrosol Manifold, cat. no. XX25 047 00, filtering clamps, cat. no. XX10 025 03, fritted glass bases with stoppers, cat. no. XX10 025 02, and glass funnels, cat. no. XX10 025 11, Millipore Corp., Bedford, MA).
k) Liquid nitrogen cold-trap system for THF collection (dewar, polypropylene 2-liter suction flask, liquid nitrogen, etc.).
l) Eyedropper.
m) Hot plate, intrinsically safe (Model HP-11515B, Sybron/Thermolyne, Dubuque, IA).
n) Teflon sheet, 0.3 to 1 mm thick (cut to fit top of hot plate).
o) Plastic petri dishes (Product no. 7242, Gelman Sciences, Ann Arbor, MI).
p) Vacuum system.

q) Freezer mill (Model no. 6700, Spex Industries, Edison, NJ).
r) Sieve, nylon, 10 µm (Spectra/Mesh N sieve, Cat. no. 08-670-205, Fisher Scientific, Springfield, NJ) or (Cat. no. 146514, Spectrum Medical Industries, Inc., Los Angeles, CA).
s) Polypropylene 250-mL wash bottle with tube cut out of top.

6.2.6. Bulk sample preparation for membrane deposition:

a) Mortar and pestle.
b) Sieve or sonic sifter: Sieve, 325-mesh, (or Model ATML3P Sonic Sifter with 325-mesh sieve, ATM Corporation, Milwaukee, WI).

6.3. Reagents (except for liquid nitrogen use reagent grade or better):

6.3.1. Sample and standards preparation

a) Tetrahydrofuran
b) Vanadium pentoxide
c) Liquid nitrogen (for vapor trap and for maintaining EDXRF SiLi detector).

6.3.2. Reagents for preparing MCA calibration sample

a) Titanium dioxide
b) Zinc oxide
c) Yttrium oxide
d) Boric acid (for secondary-target instrument)

6.4. Preparation of Standard Materials

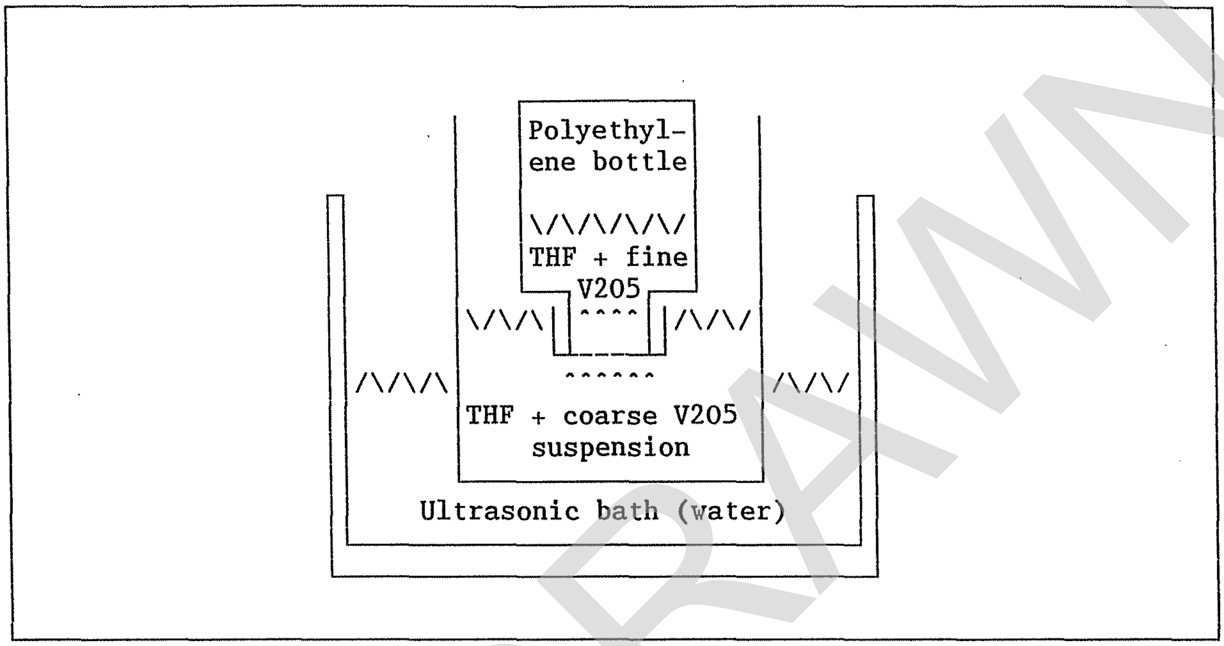
6.4.1. Use reagent grade V_2O_5 as the starting material.

6.4.2. Prepare respirable stock material by grinding reagent grade V_2O_5 in a freezer-mill operated with liquid nitrogen for 10 minutes.

6.4.3. Add this ground material to 50 to 75 mL of THF in a 100-mL glass beaker. Stir and sonicate the suspension in an ultrasonic bath.

6.4.4. Remove the tube from the cap of a 250-mL polypropylene wash bottle. Ream out a hole where the tube had been and smooth any rough edges. Prepare a sieving bottle by mounting a 10-µm nylon mesh sieve in the cap. Secure the sieve in place by screwing on the cap. Wet-sieve by first squeezing out some of the air in the bottle and inverting the bottle in the sonicated THF. A graphic representation of the standard preparation assembly is shown below:

WET-SIEVE METHOD FOR STANDARD PREPARATION



6.4.5. Isolate the dust from the suspension by removing the suspension from the bottle. Filter the dust onto a Ag membrane. A filtering apparatus similar to the one described below can be used.

6.4.6. Allow the residual THF on the dust to evaporate at room temperature. Remove the dust from the Ag membrane and store this respirable stock material in a 20-ml capped scintillation vial.

6.4.7. Assemble the filtering apparatus and liquid nitrogen cold trap, and connect to a vacuum pump. Connect the cold trap in between the filtering apparatus and vacuum pump to collect the waste THF. Any waste vapors should not enter the vacuum pump.

6.4.8. Prepare a 10 µg/mL THF-V_2O_5 suspension by weighing out 5 mg of respirable V_2O_5 stock material and quantitatively transferring it to a 500-mL volumetric flask. Dilute to volume with THF. In the same manner, weigh out 50 mg of respirable V_2O_5 and prepare a 100 µg/mL THF-V_2O_5 suspension. Add a magnetic stirring bar to each and mark the new meniscus (due to the added volume of the bar) on the neck of each volumetric flask. Sonicate 10 minutes and cool with constant stirring on a magnetic stirrer until the meniscus reaches the new mark.

6.4.9. For each standard, center a Ag membrane on the fritted-glass base of the filtering apparatus. Also center the glass chimney on top of the base and secure it with a clamp.

6.4.10. With the vacuum turned off, place 2 to 5 mL of THF in the chimney of the previously assembled vacuum filtering apparatus.

6.4.11. Turn off the stirrer and shake the suspension vigorously prior to removing each aliquot from the center of the THF suspension. Consult the following table for determining the appropriate reagent concentration and aliquot size to take in preparing each of 24 calibration standards (three standards at each of the eight levels):

Standard µg V_2O_5	Volume (mL)	Reagent Concn (µg/mL)
50	5	10
100	10	10
200	2	100
250	25	10
500	5	100
1,000	10	100
2,000	20	100
2,500	25	100

Note: Duplicate standards are prepared so that outliers may be identified and discarded. Subsequent calibrations can be performed using fewer standards at levels selected to be comparable to the samples.

6.4.12. Apply vacuum to the filtering apparatus to draw the THF through the Ag membrane. This should result in a thin, even layered deposition of the standard on the Ag membrane. Do not rinse the chimney after the material has been deposited on the membrane. Rinsing can disturb the thin layer deposition just created. Vacuum should be applied for sufficient time to dry the membrane.

6.4.13. Carefully disassemble the chimney and clamp. Remove the Ag membrane from the fritted-glass base using forceps. Do not use a fixative to secure the dust on the membranes. Place a Teflon sheet on top of an intrinsically-safe hot plate which is set at the lowest setting. Place the membrane on top of this heated Teflon sheet.

6.4.14. When dry, place the standard in a labeled petri dish.

6.4.15. Place any THF waste in an explosion-resistant metal container and dispose appropriately.

6.5. Preparation of Bulk and Air Samples

6.5.1. Bulk sample preparation:

To prevent the possibility of contaminating air samples, prepare bulk samples in an area away from where air samples are prepared; a separate filtering apparatus is recommended. Finely-divided bulk samples may be analyzed qualitatively without preparation as packed powders using XRD. If a quantitative estimate is desired, prepare as follows:

a) Bulk samples approximating respirable particle size: Weigh an aliquot of 1 to 2 mg on a PVC filter, and place in a round bottom centrifuge tube. Prepare as for air samples using the procedure in Section 6.5.2., steps 3-8.

b) Non-respirable bulks: Grind the sample to a fine powder using either a mortar and pestle or a freezer mill. Then size the sample, using a 325-mesh sieve or sonic sifter. This results in a sample particle size of less than 45 µm. Weigh out 1 to 2 mg of the sized sample on a PVC filter and place it in a round bottom centrifuge tube. Prepare as for air samples using the procedure in Section 6.5.2., steps 3-8.

6.5.2. Air sample preparation:

1) When sample weights are greater than 2.5 mg, aliquots are taken to achieve depositions within the working range.
2) Examine the filter and backup pad to determine if any breakthrough to the backup pad has occurred. If there is significant breakthrough, the sample is either not analyzed or results are reported with a disclaimer. (See Section 7.3. for reporting results.)
3) Carefully transfer the air sample (PVC filter) from the cassette to a round-bottom 40-mL centrifuge tube. Add 10 mL THF to dissolve the filter and suspend the sample. Sonicate the sample suspension for 5 to 10 min.
4) For each sample, center a Ag membrane on the fritted-glass base of the filtering apparatus. Also center the glass chimney on top of the base and secure it with a clamp.

5) With the vacuum turned off, place 2 to 5 mL of THF in the chimney of the previously assembled vacuum filtering apparatus.
6) Quantitatively transfer the suspension with rinses of THF to the glass chimney of the vacuum filtering apparatus. The total volume in the chimney should not exceed 20 mL.
7) Continue preparation of samples as described Sections 6.4.12. to 6.4.15.

6.6. XRD Calibration and Analysis

Note: The analytical procedures for XRD and XRF are written for in-house use; other equipment and data reduction systems similar to those mentioned can be used. The custom OSHA laboratory XRD software and XRD Standard Operating Procedure (SOP) (8.14., 8.15.) for data collection and reduction used in this analysis incorporate software which smoothes data, locates peaks, selects integration methods, performs weighted one- or two-piece calibrations, calculates microgram quantities, and permits analyst review and direction.

Analyze the 24 standards prepared in Section 6.4. according to the XRD SOP (8.15.). Instrument parameters (all angles are in terms of °2Θ) for calibration are:

Ag reference calibration	38.15° (primary Ag line) 44.33° (secondary Ag line)
---------------V_2O_5 scan ranges---------------	
Secondary line	30.40 to 31.70° (quantitative) (31.05° analytical peak)
Primary line	19.62 to 20.92° (qualitative)
Tertiary line	25.56 to 26.86° (qualitative)
Scan step size	0.02°
Integration time	1 to 10 s
X-ray tube power	40 kV and 40 mA

The primary or secondary Ag line is used as the reference calibration. The secondary V_2O_5 line was chosen as the quantitative line because interferences from quartz are present on the primary and tertiary lines. It is possible to make calibration curves for these two lines only if the particle-size distribution closely matches the dust used in the preparation of standards, because they are more severely affected by particle-size and preferred-orientation effects than the line at 31.05° 2Θ.

Typical scans of the three recommended analytical lines for a 250 µg V_2O_5 standard are graphically displayed in Figure 1.

Use available peak-integration or profile fitting software to obtain normalized count data. Construct a least-squares curve-fit and derive calibration coefficients for use in subsequent V_2O_5 analyses. A polynomial curve fit can be used. The presence of V_2O_5 should be qualitatively confirmed by the presence of the two additional confirmational V_2O_5 lines from the 2θ scan ranges; a strong line at 19.62 to 20.92°, and a weak line at 25.56 to 26.86°.

Consult the XRD SOP (8.15.) for further instructions.

6.7. XRF Calibration and Analysis

6.7.1. Direct-beam XRF spectrometer:

1) Consult the XRF SOP (8.16.) and power up the X-ray tube to 20 kV and 0.5 mA. Remove any filter and put the narrow collimator in place over the detector. Calibrate the element markers using a Ti-Zn-Y calibration standard consisting of a 1- to 3-mm deep equimolar mix of powdered TiO_2, ZnO, and Y_2O_3 on a 0.25 mil mylar support. Calibrate on the corresponding K_α lines at 4.508, 8.631, and 14.933 kV.

2) First analyze the standards. Next analyze the samples and repeat the standards. For each sample or standard perform the following steps:

   a) Close the shutter and open the cover.
   b) Wipe the yellow Kapton window before analyzing each sample.
   c) Place the sample face down on the yellow Kapton window over the detector, close the cover, open the shutter and initiate analysis.
   d) Label the data to identify standards and samples analyzed. Typical spectra for a 250 µg V_2O_5 standard and a blank are shown in Figure 2.

3) Save each spectrum to magnetic tape or disk (if possible). Note: On certain XRF systems without mass storage, it may be necessary to perform all the calculations after each sample is analyzed. Others allow some calculations to be

incorporated automatically in the analyses prior to saving the spectra.

6.7.2. Secondary-target XRF spectrometer:

1) Open sample chamber lid.
2) Install a Ta collimator at the detector if not already installed.
3) Install the Fe secondary target if not already installed.
4) Place Ag membranes in the autosampler. Position each sample for maximum analytical signal during analysis.
5) Close sample chamber lid.
6) Calibrate the MCA using using the Ti-Zn-Y calibration standard consisting of a pellet made of a mixture H_3BO_3 and 10-20% of an equimolar mix of powdered TiO_2, ZnO, and Y_2O_3. Calibrate on the corresponding Zn and Y K_α lines at 8.631 and 14.933 kV respectively using a Ag secondary target. One may substitute other appropriate calibration materials or secondary targets for this purpose.
7) Select the following conditions:

   Fe secondary target.
   Display range = 10 kV.
   X-ray tube power = 12 kV and 3.3 mA.
   (To reduce the affect of sum peaks, do not exceed 50% deadtime on standards or samples.)
   Atmosphere = Vacuum.
   Acquisition time = 600 s.
   Analyze a Lucite monitor sample or other appropriate monitor sample to adjust for varying X-ray tube output.

8) Analyze all standards and samples.
9) Save spectra to magnetic tape or disk. Note: On certain XRF systems it may be convenient to perform escape and sum peak corrections operations prior to saving each spectrum.

7. Calculations

7.1. XRD Data Reduction

The XRD results from line to line may not agree well. Use the 2° line results for calculations unless interferences are present. After calibration and analysis, calculate the microgram quantities of the analyte from the calibration curve. Tne V_2O_5 exposure is estimated using the following equation:

Vanadium pentoxide exposure (As V_2O_5 in mg/m³) = A/B

A = µg V_2O_5 found (blank subtracted)
B = sample air volume in liters

7.2. XRF Data Reduction

Use software features available on instrument:

7.2.1. Recall spectrum.

7.2.2. Remove escape peaks.

7.2.3. Remove sum peaks.

7.2.4. Identify V lines and any interfering elements.

7.2.5. Perform background corrections.

7.2.6. Perform profile fit or Gaussian deconvolution of the identified lines.

7.2.7. Tabulate integrated peak counts and masses of standards.

7.2.8. Use the count (or count rate) data to construct a least-squares curve-fit and derive calibration coefficients for use in subsequent V_2O_5 analyses. A polynomial curve fit can be used. Use the concentration-response curve to calculate the µg of analyte present. The V_2O_5 exposure is calculated as in Section 7.1.

7.3. Reporting Results

Compare the XRD and XRF results. As previously mentioned (Section 3.3.), particle-size and preferred-orientation effects may cause the XRD results to differ from the XRF results by as much as a factor of two. The XRD results are used as confirmation. If V is found by XRF and V_2O_5 is not confirmed by XRD, the analyst may wish to identify the vanadium-containing species using XRD wide-angle scans and a XRD line library similar to what is mentioned in Section 6.2.4.

If a reasonable comparison is obtained between XRD and XRF, report results to the industrial hygienist as mg/m³ V_2O_5.

Do not report XRD quantitative results; XRF results represent more reliable estimates of the amounts of V_2O_5 potentially present. Results by XRD represent estimates only.

Disclaimers:

Particulate present on the backup pad constitutes some sample loss. Occasionally this may be seen and can be due to a poor cassette seal on the filter, improper positioning of the filter in the cassette, or poor quality control of the filter and/or cassette. If this type of contamination occurs, relay a note to the compliance officer indicating that some of the sampled material was found on the backup pad and the reported value may be lower than the actual exposure.

8. References

8.1. **Carsey, T.P.:** Quantitation of Vanadium Oxides in Airborne Dusts by X-ray Diffraction. Anal. Chem. 57:2125-2130 (1985).

8.2. **National Institute for Occupational Safety and Health:** Collaborative Tests of Two Methods for Determining Free Silica in Airborne Dust (DHHS Publication No. 83-124). Cincinnati, OH: National Institute for Occupational Safety and Health and Bureau of Mines, 1983.

8.3. **National Institute for Occupational Safety and Health:** NIOSH Manual of Analytical Methods, 3rd. ed., Cincinnati, OH: National Institute for Occupational Safety, 1986. pp. 7504-1 to 7504-10.

8.4. **Windholz, M.; ed.:** The Merck Index. 10th ed., Rahway, NJ: Merck and Co., 1983. p. 1417-1418.

8.5. **American Conference of Governmental Industrial Hygienists:** Documentation of the Threshold Limit Values and Biological Exposure Indices (Pub. No. ISBN: 0-036712-68-6). Cincinnati, OH: American Conference of Governmental Industrial Hygienists, 1986. p. 620.

8.6. **National Institute for Occupational Safety and Health:** Criteria for a Recommended Standard ... Occupational Exposure to Vanadium (DHEW/NIOSH Pub. No. 77-222). Washington, D.C., U.S. Government Printing Office, 1977. pp. 21-44.

8.7. "Air Contaminants; Final Rule" Federal Register 54:12 (19 Jan. 1989). pp. 2475-2476.

8.8. **Occupational Safety and Health Administration Analytical Laboratory:** OSHA Manual of Analytical Methods edited by R.G. Adler (Method No. I-1). Salt Lake City, UT. 1977.

8.9. **Occupational Safety and Health Administration Technical Center:** Metal and Metalloid Particulates in Workplace Atmospheres (ICP Analysis) by J.C. Septon (USDOL-OSHA-SLTC Method No. ID-125G). Salt Lake City, UT. Revised 1991.

8.10. **Occupational Safety and Health Administration Technical Center:** Vanadium Pentoxide Backup Data Report (ID-185) by M.C. Rose. Salt Lake City, UT. Revised 1991.

8.11. **Occupational Safety and Health Administration Analytical Laboratory:** OSHA Analytical Methods Manual (USDOL/OSHA-SLCAL Method No. ID-142). Cincinnati, OH: American Conference of Governmental Industrial Hygienists (Pub. No. ISBN: 0-936712-66-X), 1985.

8.12. **Occupational Safety and Health Administration Analytical Laboratory:** OSHA Analytical Methods Manual (USDOL/OSHA-SLCAL Method No. ID-143). Cincinnati, OH: American Conference of Governmental Industrial Hygienists (Pub. No. ISBN: 0-936712-66-X), 1985.

8.13. **American Conference of Governmental Industrial Hygienists:** Threshold Limit Values and Biological Exposure Indices for 1989-1990 (Pub. No. ISBN: 0-936712-81-3). Cincinnati, OH: American Conference of Governmental Industrial Hygienists, 1989.

8.14. **Occupational Safety and Health Administration Analytical Laboratory:** X-ray Diffraction Program Documentation. Salt Lake City, UT. 1981 (unpublished).

8.15. **Occupational Safety and Health Administration Technical Center:** Standard Operating Procedure (XRD). Salt Lake City, UT. In progress (unpublished).

8.16. **Occupational Safety and Health Administration Analytical Laboratory:** Standard Operating Procedure (XRF). Salt Lake City, UT. 1981 (unpublished).

Table 1
Potential Vanadium XRF Line Interferences
(Not shown to scale.)

Interference	Line ID. = Energy (kV)=	V Kα 4.949	V Kβ 5.427
Sn LI ab	4.464		
Ba $L_{\alpha1}$	4.467		
Ti K_{α}	4.508		
I $LIII_{\beta2}$	4.507		
I LIII ab	4.559		
Te $LII_{\lambda1}$	4.570		
Te LII ab	4.613		
S 2 x K_{α} sum peak	4.614		
Cs $LII_{\beta1}$	4.620		
Fe K_{α} Si escape peak	4.64		
La $LIII_{\alpha1}$	4.651		
Sb LI ab	4.697		
S K_{α} + K_{β} sum peak	4.775		
I $LIII_{\lambda1}$	4.800		
Ba $LII_{\beta1}$	4.828		
Ce $LIII_{\alpha1}$	4.840		
I LII ab	4.856		
Ti K_{β}	4.931		
Cs $LIII_{\beta2}$	4.936		
S 2 x K_{β} sum peak	4.936		
Te LI ab	4.938		

(CONTINUED)

The L lines for the noble gas xenon (Xe) and the short-lived radioactive element promethium (Pm) were not considered due to their extremely low probability of occurrence in compliance samples.

Table 1 (Cont.)

Potential Vanadium XRF Line Interferences
(Not shown to scale)

Line ID. = V Kα, V Kβ
Energy (kV)= 4.949, 5.427

Interference	Energy (kV)
Cs LIII ab	5.011
Pr $LIII_{\alpha1}$	5.034
La $LII_{\beta1}$	5.043
Ba $LIII_{\beta2}$	5.156
Co K_{α} Si escape peak	5.16
I LI ab	5.190
Nd $LIII_{\alpha1}$	5.230
Cl 2 x K_{α} sum peak	5.244
Ba LIII ab	5.247
Ce $LII_{\beta1}$	5.262
Cs $L_{\lambda1}$	5.280
Fe K_{β} Si escape peak	5.30
Cs LII ab	5.358
La $LIII_{\beta2}$	5.384
Ag sum peaks	5.266 - 7.038
Cr K_{α}	5.41
Cl K_{α} + K_{β} sum peak	5.439
Pr $LII_{\beta1}$	5.489
La LIII ab	5.489
Ba $LII_{\lambda1}$	5.531
Ba LII ab	5.623

The L lines for the noble gas xenon (Xe) and the short-lived radioactive element promethium (Pm) were not considered due to their extremely low probability of occurrence in compliance samples.

Table 1 (Cont.)

Potential Vanadium XRF Line Interferences
(Not shown to scale)

Interference	Line ID. = Energy (kV)=	V Kα 4.949	V Kβ 5.427	
Cl 2 x K_β sum peak				5.634
Sm $L_{\alpha 1}$				5.636
Cs LI ab				5.720
Ce LIII ab				5.729

The L lines for the noble gas xenon (Xe) and the short-lived radioactive element promethium (Pm) were not considered due to their extremely low probability of occurrence in compliance samples.

CONFIRMATION OF VANADIUM PENTOXIDE IN WORKPLACE ATMOSPHERES

Analytical Peaks for X-Ray Diffraction (250 µg V_2O_5 Standard)

```
SAMPLE WT.= 250.     UG

AG CAL. 27778   COUNTS AT  38.13 DEG.

PEAK =       31.06  PEAK =        20.32  PEAK =        26.18
LOW LIMIT =30.54    LOW LIMIT =19.68     LOW LIMIT =25.68
UP LIMIT = 31.64    UP LIMIT = 20.88     UP LIMIT = 26.80
INT TIME = 1        INT TIME = 1         INT TIME = 1
NORM CNTS =4642     NORM CNTS =16889     NORM CNTS =3038
```

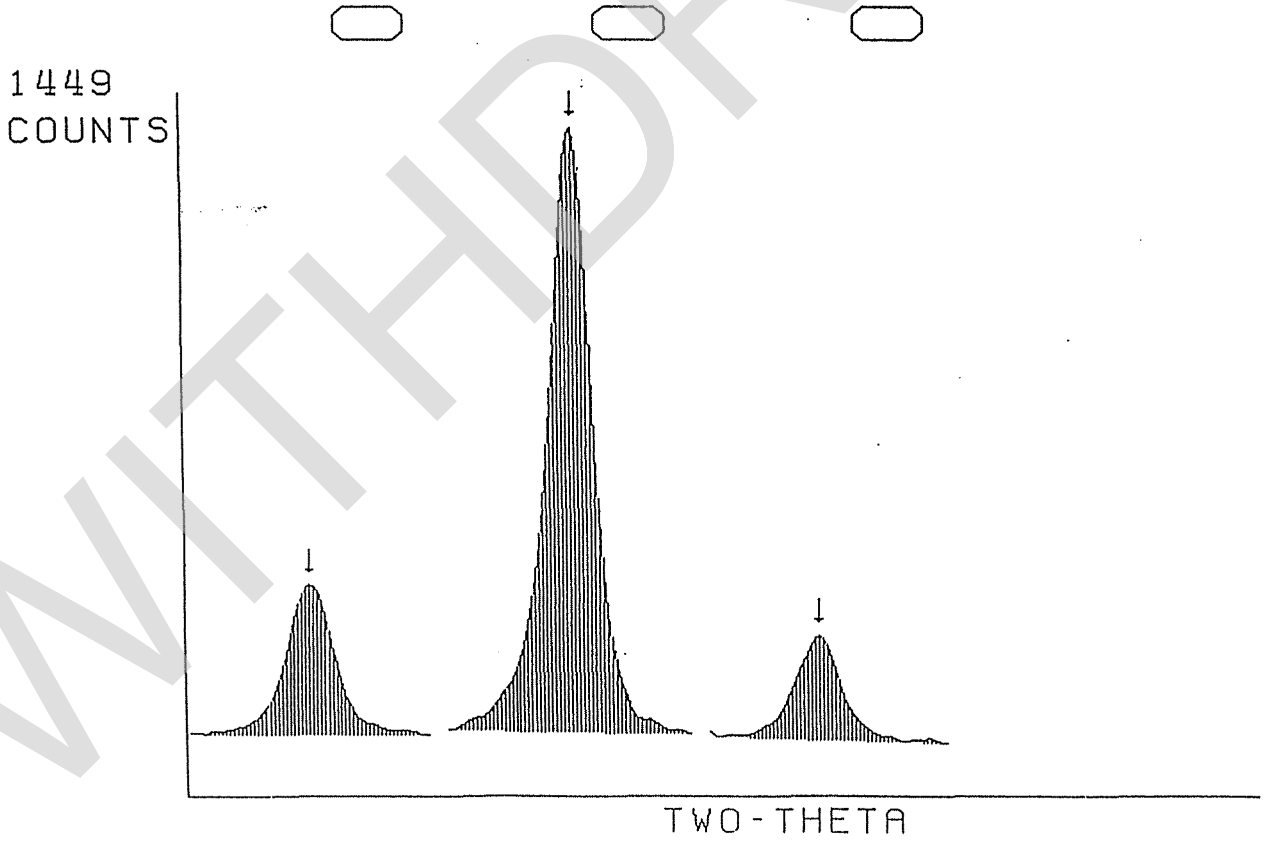


Figure 1

CONFIRMATION OF VANADIUM PENTOXIDE IN WORKPLACE ATMOSPHERES

Analytical Peaks for X-Ray Fluorescence (250 µg V205 Standard)

COMMENTS

50µg V_2O_5 STD = V250C13BR

BLANK = VBLG

ANALYST Mike Rose
DATE 3/13/87
COLLIMATOR Narrow
SECONDS 100
% DEAD TIME <10

SAMPLE # V250C13BR/VBLG
KV = 20 MA = 0.5
VACUUM = AIR TO
FILTER = NONE
VERT. SCALE = 256
HOR. SCALE = FULL
SMOOTHED 0 times

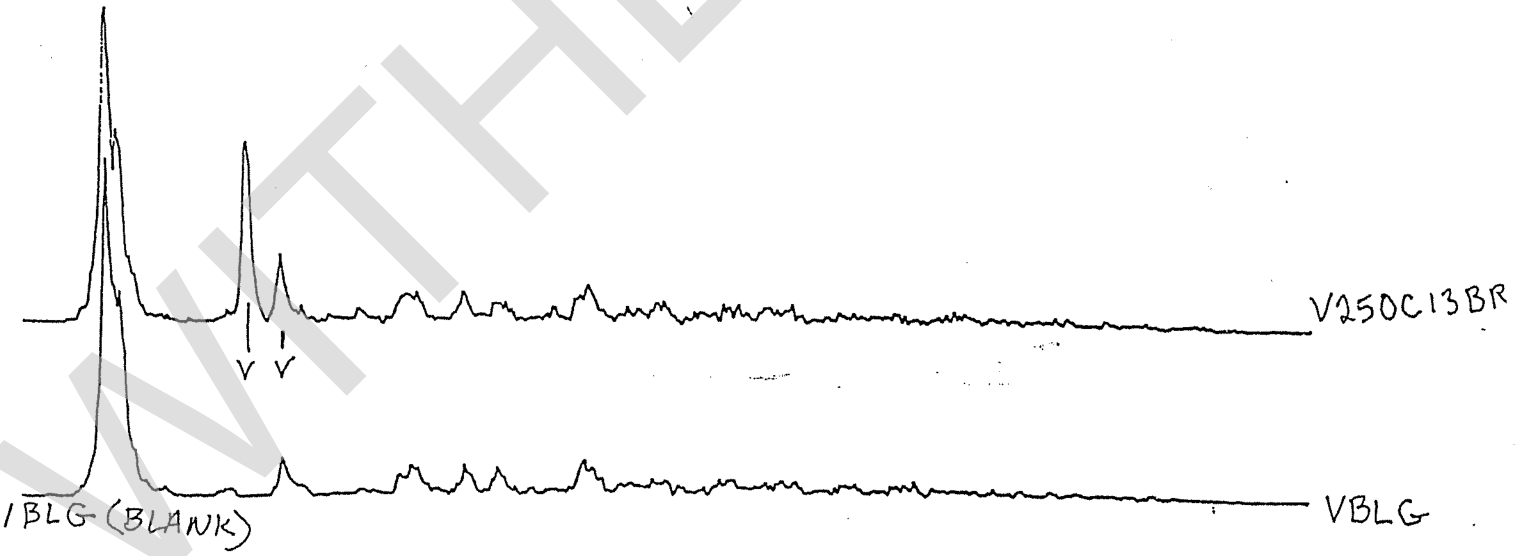


Figure 2