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Preparation of Standards for Valence State Measurements by X-Ray Fluorescence

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PREPARATION OF STANDARDS FOR VALENCE STATE MEASUREMENT BY X-RAY FLUORESCENCE

by

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ABSTRACT

The preparation and characterization of standard samples representing several valence states for sulfur, vanadium and chromium is described. These standards will be used by the U.S. Environmental Protection Agency, which is investigating the potential for determining valence state by high resolution wavelength dispersive x-ray emission analysis. A total of forty (40) single state and thirteen (13) multistate standards were prepared by dust generation and collection on polycarbonate filters. The prepared samples and valence states include sulfur (0, +4, +6, -2), vanadium (0, +4, +5) and chromium (+3, +6). At least three standards were prepared for each valence state, with mass concentration of the valence state element in the range 1 to 50 $\mu g/cm^2$. The prepared samples were coated with a thin layer of nitrocellulose by a wicking procedure to provide a protective coating and to prevent loss of material. Representative samples were analyzed for the uniformity of the deposit, mean particle size and stability in air and x-ray irradiation. Duplicate samples of each standard have been delivered to the Environmental Protection Agency.

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SECTION 1

INTRODUCTION

The relative toxicity of various compounds depends largely on the valence state of the elements. Most analytical methods used to characterize source emission samples are quantitative for specific elements, but provide no information about valence state or the form of chemical combination. X-ray diffraction can identify specific compounds present in a sample, thus identifying valence state. However, the technique is limited to major, crystalline phases present in amounts >50 to 100 μg per square centimeter of filter and thus is generally not suitable for source emission samples.

The energy of outer-shell (valence) electrons of an element is altered when the element combines with others to form a compound. Soft x-ray spectra associated with valence electron transitions are likewise altered as a result of chemical combination, losing the discrete energy characteristics of an atomic orbital and assuming an energy band, the nature of which is dependent upon the configuration of the molecular orbital. The "fine structure" of the spectral band provides specific information about valence state of the elements. The measurement of x-ray emission lines, as applied to chemical bonding, is applicable only to transitions in the outer orbitals and hence, involves long wavelengths. Special x-ray analysis apparatus is needed to measure these wavelengths.

The Environmental Protection Agency requires the preparation of valence state standards to evaluate and calibrate methods which employ high resolution wavelength dispersive x-ray fluorescence spectrometry to determine various chemical oxidation states of elements of environmental concern in pollution samples. The present program was undertaken to prepare standard samples of sulfur, vanadium and chromium in various valence states. The scope of work for this study is as follows:

The contractor shall prepare standards meeting the following criteria:

1. Single and multistate standards for three elements shall be prepared: sulfur, vanadium and chromium.

    a. The sulfur standards shall include the following species: elemental, sulfite, sulfate, and sulfide.

    b. The vanadium standards shall include oxidation states represented by: V, VO_2, and V_2O_5.

    c. The chromium standards shall include oxidation states represented by: Cr_2O_3 and CrO_3.

d. Compounds other than oxides may be used.

2. Single (containing only one of the valence species) standards shall be prepared at three concentrations ranging from 1 micrograms/cm^2 to 50 micrograms/cm^2 for each oxidation state.

3. Multi-state standards shall be prepared consisting of combinations of oxidation states of a given element on the same specimen. Chemical reactivity may make this impossible with some combinations.

4. Total deposition (loading) on each standard shall be limited to 500 micrograms or less per square centimeter.

5. Samples shall be uniformly dispersed over a circular area of at least 30 mm diameter at the center of a 47 mm substrate.

6. Due to high instability of some species, a method for stabilizing the reactive oxidation states shall be developed.

7. Stability of the samples shall be demonstrated. This includes exposure to x-ray tube primary radiation.

8. Duplicate sets of all standards shall be delivered to EPA, Research Triangle Park, NC.

The end product of this program is the delivery of replicate sets of single and multistate standards of sulfur, vanadium and chromium compounds to the Environmental Protection Agency.

SECTION 2

CONCLUSIONS

The present program was conducted to generate standard samples of various valence states for sulfur, vanadium and chromium for use by the Environmental Protection Agency in determining the valence state of these elements when found in source emission samples. A total of forty (40) single state and thirteen (13) multistate standards have been prepared, consistent with the program requirements. Based upon the evaluation of proposed standard samples, the following conclusions were reached:

- It is possible to prepare valence state standards of sulfur, vanadium and chromium compounds (representing those that may be encountered in source emission samples) by collection on filter substrates in a dust generation apparatus using selected compounds as the source material.
- Elemental valence state mass concentrations of $\sim$1 to 50 $\mu g/cm^2$ can be prepared.
- Long-term stability of prepared standards to atmospheric exposure and x-ray irradiation has been demonstrated for samples protected by coating with a layer of nitrocellulose.
- Replicate standards prepared on 47 mm diameter polycarbonate filters have been prepared at concentrations ranging from 0.1 to >50 $\mu g/cm^2$ for the following elements and valence states:

S: 0, -2, +4, +6

V: 0, +4, +5

Cr: +3, +6

SECTION 3

RECOMMENDATIONS

A total of fifty-three (53) standards representing various valence states of sulfur, vanadium and chromium, have been delivered to the Environmental Protection Agency (EPA). The following additional studies are recommended:

- Carry out measurements of the elemental mass concentration for the various standard samples, by x-ray emission analysis, including measurements of S, V and Cr (and other elements that are present, such as La, Pb and Ba), using appropriate calibration samples. Determine the agreement between prepared and measured concentrations. It is expected that these analyses will be made by the EPA.

- Using a high resolution x-ray spectrometer, measure the x-ray spectra (sensitive to valence state) for the standards and determine the suitability of these standards for estimating the valence (oxidation) states of sulfur, vanadium and chromium present in source emission samples.

- Based upon the above, prepare additional standards for other combinations of valence state and mass concentration.

SECTION 4

COMPOUND SELECTION

The program scope of work specified the preparation of standards representing several oxidation states for sulfur, vanadium and chromium, including some multistate standards. It is expected that these standards will be useful for determining the suitability of research-type spectrometers to detect a difference in spectra for the various states at the concentration levels of interest. Once such an instrument is identified or developed, additional valence state standards and various combinations of multistate standards can be prepared.

It was agreed to prepare standards for the four oxidation states of sulfur and for fewer oxidation states for vanadium and chromium. After consultation with the Project Officer, it was agreed to prepare three oxygen states for vanadium, including the pure element, and two for chromium. In the case of chromium compounds, the +6 state is recognized as being especially toxic. CrO_3 is not stable at elevated temperatures, transforming to Cr_2O_3. However, the +6 state should be retained by formation of a salt, such as $PbCrO_4$. A list of the oxidation states for which standards were to be prepared, together with a selection of candidate compounds, is given in Table 1.

The specific compounds to be used in the standards for all three elements were selected, as far as possible, with emphasis on the likelihood of occurrence in stack emission samples and on their relative stability. All compounds except for the mercury sulfite complexes and the barium and lanthanum sulfite salts, are available in powder form from commercial sources.

TABLE 1. CANDIDATE COMPOUNDS FOR VALENCE-STATE STANDARDS

Element	Valence (Oxidation) State	Compounds/Comments
Vanadium	0	V metal, powder (or as wire for vapor deposition)
	+4	V_2O_4, powder
	+5	V_2O_5, most stable oxide
Chromium	+3	Cr_2O_3, powder, most stable oxide
	+6	$PbCrO_4$, powder
Sulfur	0	Sublimed sulfur ("flowers")
	-2	Most likely as sulfide of cadmium (CdS), mercury (HgS) or lead (PbS); there may be some stability problem due to air oxidation, and all three compounds may have to be tested.
	+4	This oxidation state is the most difficult to stabilize; complex salts such as $Hg(SO_3)_2^{-2}$ are known to be very stable to oxidation in solution, and are potentially useful if they can be prepared as solid salts; sulfite salts of barium ($BaSO_3$) or lanthanum ($La_2(SO_3)_3$) may be stable although recent studies at Arthur D. Little, Inc. show that the corresponding calcium salts are oxidized rather easily in air.
	+6	$BaSO_4$, powder

SECTION 5

EXPERIMENTAL PROCEDURES AND RESULTS

STARTING MATERIALS

Valence State Compounds

Approximately 100g (or greater) samples were ordered for each of the candidate valence state compounds, except for S^{+4}. The powders utilized for the preparation of standards are identified in Table 2. Each of the compounds was initially evaluated by optical microscopy to estimate the particle size distribution and by x-ray methods to determine the presence of secondary elements and phases. The results of these evaluations are summarized in Table 3. Second procurements of PbS and $BaSO_4$ from other sources contained similar impurities as the first procurement; these compounds were accepted for use despite the minor phase and element interference. A second phase was observed in the V_2O_4 sample. Although it could not be identified, the absence of trace elements suggests that it is a higher oxidation state of vanadium (not V_2O_5), estimated to be about 5 percent. Based on phase stability after several weeks exposure to laboratory air, this compound was accepted for standard preparation.

In many cases, the compounds contained fairly large particles or agglommerates. Although the latter would tend to break down by air jet milling during sample generation, it was decided to use an impactor stage having approximately a 4 μm - 50% cutoff at the entrance to the sample generation chamber, (Appendix A), to minimize the presence of large particles on the filter standards.

With respect to the S^{+4} standard, initial attempts to prepare a mercurisulfite complex standard by reacting $HgCl_2$ and NaCl with Na_2SO_3 were unsuccessful due to oxidation of the product to sulfate. Therefore, attempts were initiated to prepare lanthanum sulfite by reaction of $LaCl_5 \cdot 5H_2O$ and $NaSO_3$. The $La_2(SO_3)_3$) precipitate was carefully vacuum filtered and washed and then placed in a dessicator under argon to minimize oxidation. An aliquot of the wet solid was analyzed for total oxidizable sulfur by I_2 titration, and another aliquot of dry solid was similarly analyzed. No differences were observed. An analysis of the La/SO_3 ratio indicated no difference between the wet and dry solids. Therefore, it appeared that there is no oxidation of the sulfite during drying. A second 50g sample was prepared, and x-ray diffraction analysis indicated that the material was fully reacted (there was no $LaCl_3$). On the basis of a consistent x-ray diffraction pattern after a two-week exposure to laboratory air and a lack of detectable sulfate by chemical analysis, the prepared $La_2(SO_3)_3$ powder was determined to be stable and was accepted as the S^{+4} standard.

TABLE 2. IDENTIFICATION OF VALENCE STATE COMPOUNDS

Element/ Valence State	Compound	Supplier	Grade	Particle Size	Lot Number
S°	S	Fisher	Laboratory	Powder	704110
S^{-2}	PbS	Fisher	Science	Powder	L173
S^{+4}	$La_2(SO_3)_3$	ADL	Experimental	Powder	-
S^{+6}	$BaSO_4$	Fisher	Reagent	Powder	-
V°	V	Alfa	-	-325	012177
V^{+4}	V_2O_4	Alfa	-	Powder	040777
V^{+5}	V_2O_5	Fisher	Certified	Powder	730793
Cr^{+3}	Cr_2O_3	Alfa	-	-325	042077
Cr^{+6}	$PbCrO_4$	Fisher	Certified	Powder	5363

TABLE 3. CHARACTERIZATION OF AS-RECEIVED COMPOUNDS

Compound	Secondary Phases (X-Ray Diffraction)	Minor Elements (X-Ray Fluorescence)	Particle Size* (Optical Microscopy)
S	-	-	8-10 μm
PbS	2% $PbSO_4$	I (trace)	1, 10 (B)
$La_2(SO_3)_3$	-	-	-
$BaSO_4$	-	Sr	2-5 (A)
V	-	-	4, 20 (B)
V_2O_4	5% second phase	-	1-3
V_2O_5	-	-	1-3
Cr_2O_3	-	-	2-5 (A)
$PbCrO_4$	-	-	3-5 (A)

*A - Agglormerates up to 50 μm also present
B - Biomodal size distribution

Filter Media

Candidate filter media were evaluated for stability to x-ray radiation. For this purpose, membrane filters of polycarbonate, mixed esters of cellulose and a copolymer of acrylonitrite and vinylchloride were exposed to radiation from a chromium target x-ray tube operated at 45 KV and 20 ma for a period of ten hours. The area of x-ray illumination was well defined by the development of a light brown color in the filters. Flexure tests after exposure showed severe embrittlement to the mixed esters and copolymer filters and slight embrittlement to the polycarbonate filter. Subsequently, a set of Teflon-on-Teflon filters were obtained and similarly evaluated. These filters were the least stable to x-ray irradiation, splitting after 3 hours exposure time. A summary of the filter evaluation studies is given in Table 4.

Although quite fragile and subject to electrostatic charging effects, the polycarbonate filters appear to be the best substrate material for the valence state standards and were used throughout the program.

SAMPLE PREPARATION

All standards were prepared in a dust generation system (FRED) described in Appendix A. After preliminary runs, FRED was fitted with two stages of a cascade impactor to provide a particle size distribution with an upper size cutoff of approximately 4 μm (50 percent cutoff, aerodynamic diameter). The 12 available sample ports were modified to hold six 47 mm diameter filter cassettes alternately with six 25 mm diameter filter cassettes. The smaller filters were generally used for chemical analysis (usually four filters) and for x-ray analysis and microscopic characterization. The 47 mm filters were preserved as standards, although they were occasionally analyzed to check agreement with the 25 mm diameter filters.

At the beginning of the program a series of six 47 mm and six 25 mm filters from the same run (with elemental sulfur) were analyzed to determine the equivalence of collected masses on the two size filters. The results were as follows:

	Filter	Mass S° (g)		Filter	Mass S° (g)
Large	1	313	Small	1	346
(47 mm)	2	289	(25 mm)	2	250
	3	271		3	338
	4	280		4	258
	5	274		5	275
	6	283		6	(Sample Lost)
	Mean	285		Mean	293
	CV	0.053		CV	0.155

TABLE 4. X-RAY STABILITY OF FILTER SUBSTRATES*

Filter Material	Supplier	Designation	Pore Size (μm)
Polycarbonate	Nuclepore	-	0.4
Mixed Esters Cellulose	Millipore	AA	0.8
Acrylonitrile/ Polyvinylchloride Copolymer	Gelman	DM 450	0.45
Teflon-on-Teflon	Ghia	P147-PL02	2

*All filters were 47mm in diameter

The results are statistically equivalent, although a somewhat poorer coefficient of variation is noted for the 25 mm diameter set. This may be the result of anisokinetic sampling due to the relatively small diameter of the filter holder opening.

For each standard, the first run was targeted for the heavy concentration level (50 μg of the valence state element per square centimeter) with mass loadings determined by gravimetric analysis. Adjustments in the Wright dust feed gear settings and collection time was then used for setting conditions for the other desired concentration levels (1 and 10 μg element/cm^2).

SAMPLE ANALYSIS

Valence/element and total mass concentration was determined for each sample set by the analysis of at least four filters (two filters were used for some of the multistate standards). The mean mass (μg) of the measured element was used to calculate the mass concentrations, with the effective area of the 47 mm diameter filter taken as 13.85 cm^2.

Analysis Procedure

S° - Sulfur--

Elemental sulfur was analyzed by the thiocyanate/acetone colorimetric technique*. For this purpose the filters are leached with a solution of acetone and water (95% acetone by volume), then reacted with cyanide to give thiocyanate. This is measured colorimetrically after addition of an acetone solution of ferric chloride. The procedure is as follows:

The filters are placed in screw cap jars, an appropriate amount of 95% acetone (usually 25 ml) is added, and the jar sealed using a sheet of teflon to prevent contact with the cap. The filters are leached for at least one hour, then an aliquot containing between 2 and 200 micrograms of sulfur is removed and reacted with 5 ml of 0.1% NaCN (in 95% acetone). The volume is made up to 25 ml and is allowed to stand 5 minutes.

A 5 ml aliquot is then taken and mixed with 5 ml of 0.2% $FeCl_3$ solution. The absorbance of the resulting ferrithiocyanate (corrected for the reagent blank) is measured at 465 μm, using 1cm cells in a Coleman Model 55 UV-Visible Spectrophotometer.

Filter blanks and spiked filters are run initially to ensure that interferences are not present and that recovery of S° from the filter is 100%. A calibration curve is generated during each set of analyses.

*Skoog and Bartlett, Analytical Chemistry 26, 1954, 1008-1011.

S^{-2} - PbS--

Lead content was measured by atomic absorption spectrophotometry. The lead sulfide samples were digested in hot concentrated hydrochloric acid. They were then diluted as required for analysis, and aspirated into a Perkin-Elmer Model 503 spectrophotometer. Appropriate standards were prepared and analyzed for a calibration curve. Recovery of filter spikes was checked and found to be 97.6%.

S^{+4} - $La_2(SO_3)_3$--

Lanthanum content was measured by plasma emission spectrophotometry (Spectrophotometrics DC-Arc Plasma Spectrophotometer). The lanthanum sulfite samples were digested in hot 10% HCl for 2 hours and diluted as required for analysis. Appropriate standards were prepared and analyzed for a calibration curve. Recovery was found to be 100%.

S^{+6} - $BaSO_4$--

Barium content was analyzed by plasma emission spectrophotometry. The barium sulfate samples were desorbed in 20 ml of a mixture of 10 parts concentrated ammonium hydroxide and 90 parts 0.1 N EDTA. The samples were warmed gently to dissolve the barium sulfate and then diluted as required for analysis. The samples were aspirated into a Spectrophotometrics DC-arc plasma spectrophotometer. Appropriate standards were prepared and analyzed for a calibration curve. Recovery was checked and found to be 97.9%.

V° - Vanadium--

Vanadium content was analyzed by atomic absorption spectrophotometry. Some difficulty was encountered in desorbing the vanadium metal from the Nuclepore filter. Recoveries of only 44% were observed with 0.1 N nitric acid. Therefore, hot concentrated nitric acid was used to desorb the material. Great care had to be taken to prevent the filters from curling during the digestion process. The samples were diluted as necessary and aspirated into a Perkin-Elmer Model 503 Spectrophotometer. Recovery was found to be approximately 100%.

V^{+4} - V_2O_4--

Vanadium content was determined by atomic absorption spectrophotometry. The vanadium oxide samples were digested in hot concentrated nitric acid, diluted as required for analysis and aspirated into a Perkin-Elmer Model 503 Spectrophotometer. Appropriate standards were prepared and analyzed for a calibration curve. Recovery was checked.

V^{+5} - V_2O_5--

Atomic absorption analysis of vanadium was carried out by dissolving the V_2O_5 from the filter in 0.1 N HCl at about 80°C. Samples were diluted as appropriate and aspirated or injected into a nitrous oxide/acetylene flame

or graphite tube, respectively, depending on the concentration. Appropriate standards and blanks were run along with the unknowns.

Cr^{+3} - Cr_2O_3--

The chromium content was analyzed by atomic absorption spectrophotometry. The chromium oxide samples were digested in a mixture of hot concentrated nitric acid and concentrated hydrochloric acid. They were then diluted as required for analysis and aspirated into a Perkin-Elmer Model 503 spectrophotometer. Appropriate standards were prepared and analyzed for a calibration curve. Recovery was checked and found to be 95.4 percent.

Cr^{+6} - $PbCrO_4$--

Chromium content was analyzed by atomic absorption spectrophotometry. The samples were desorbed in 0.1 N HCl at about 80°C and after appropriate dilution, were aspirated into a nitrous oxide/acetylene flame for analysis. Appropriate standards and blanks were run along with the unknowns.

S^{-2}, S^{+6} - PbS, $BaSO_4$--

Duplicate filters were analyzed for lead content by digestion in concentrated nitric acid and measurement by DC arc plasma emission spectroscopy. A second set of duplicate samples were analyzed for barium content by the procedure given above. Sulfur content for the two valence states were calculated based on the measured metal content and stoichiometry.

V°, V^{+5} - Vanadium, V_2O_5--

Duplicate filters were analyzed for V_2O_5 content by polarography. A 5 ml aliquot of 1M NH_4Cl adjusted to pH 9.9 with conc. NH_4OH was added to extract the V_2O_5. The material dissolved readily (within one minute) and in no case was any suspended material noticed. An aliquot of the extract was added to 5 ml of the buffer (pH 9.9) and the differential pulse polarogram was taken. The height of the peak at -1.27V was taken as a measure of the V_2O_5 concentration. A standard curve was prepared covering the range of 1-12 µg of V (added as V_2O_5) in 5 ml buffer. The standard stock solution was stable for at least 5 hours. The sensitivity of the procedure is 0.32 µA per 1 µg V(V_2O_5) in 5 ml solution (3.9×10^{-6}M Vanadium).

Some preliminary experiments were made to determine if the presence of V, V_2O_3 and V_2O_4 would interfere in the procedure.

> For V metal: 9.3 mg V was added to 5 ml of the buffer and extracted for 20 minutes. The resulting suspension was allowed to settle and the supernatant analyzed. A total of 112 ± 10 µg V (as V_2O_5) was found. This is equivalent to only 1.2% of the V present as V_2O_5.
>
> For V_2O_4: 10 mg was added to 5 ml of buffer. Very little of the material dissolved in 10 minutes. The resulting solution yielded 309 µg V present as V_2O_5 (5.0% of V).

For V_2O_3: 5 mg was dissolved in 5 ml of buffer. The solution gave a weak wave at -1.175V and showed no V_2O_5. The response was only ∿5% that of a similar concentration of V_2O_5.

These experiments indicate that the presence of these other species on the filter would contribute little to the V_2O_5 signal if they were present at comparable levels.

Total vanadium was determined by digestion in concentrated nitric acid and analysis by plasma emission spectroscopy.

Cr^{+3}, Cr^{+6} - Cr_2O_3, $PbCrO_4$--

Mixed phase standards for Cr^{+3} (Cr_2O_3)/Cr^{+6} ($PbCrO_4$) were analyzed by atomic absorption spectrophotometry using the procedures described above for the individual valence states.

Experimental Results

The experimental results, including valence state/element total mass concentrations are given for the single and multistate standards in Tables 5 and 6, respectively. The forty (40) single state standards range in concentration from 0.094 to 75 μg/cm^2 (valence state/element) and 1 to 512 μg/cm^2 (total). The thirteen (13) multistate standards range in valence state/element concentration from 1 to 74 μg/cm^2, with total mass concentration ranging up to 200 μg/cm^2.

SAMPLE PROCESSING AND EVALUATION

Mounting and Coating

Sample holders designed to contain 47 mm diameter filters and to be used in the EPA's x-ray apparatus were supplied by the EPA. Before mounting, the samples were coated with a thin layer of nitrocellulose (Parlodian) to provide protection from the atmosphere (to minimize the opportunity for oxidation) and to prevent the loss of material. For this purpose, a 0.6 cm thick pad of polyurethane is placed in a 10 cm Petri dish and filled with a 0.5 percent solution of nitrocellulose in amyl acetate to the top of the polyurethane. Pieces of 10 cm diameter filter paper (such as Whatman 41) are placed on the polyurethane pad. Three to five seconds are required to wet the top piece with the nitrocellulose solution. The filter to be treated is placed particle side up on a clean 5 cm diameter filter paper, which is placed on the stack. After coating (requiring about 5 seconds), the 5 cm diameter filter is removed and placed aside. After some drying (about 30 seconds), the filter is picked up with tweezers, held until almost dry (20-30 seconds) and placed in the holder. The slightly wet periphery of the filter will adhere to the mounting ring when dry.

At the slow wicking rates employed, there was no evidence for particle migration to the clean edge of the filter. After drying, heavily loaded samples could be treated quite aggressively with no loss of material. To determine the increase in mass due to treatment, three clean Nuclepore filters were weighed before and after parlodian treatment; the change in weight,

TABLE 5. MASS LOADINGS OF SINGLE PHASE VALENCE STATE STANDARDS

Set No.	Element/ Valence State	Compound	Date Generated	Mass Concentration*			
				N	MZ	MT	CV
9a	S°	S	12-20-77	4	54.0	54.0	14
9b				4	9.5	10	19
9c				4	0.69	1	46
10	V^{+5}	V_2O_5	12-30-77	4	75.8	136	10
11			1-04-78	2	42.2	75	16
12				4	6.56	11	17
13				4	0.92	2	16
15	Cr^{+6}	$PbCrO_4$	1-17-78	4	27.6	163	5
16				4	4.01	24	4
17				4	0.46	3	4
18			1-19-78	4	59.6	353	1
20	V°	V	1-25-78	2	25.6	26	4
21				3	17.5	18	9
22			1-26-78	2	1.13	1	17
24				3	32.3	32	2
25			2-03-78	3	37.5	37	10
26				4	7.87	8	13
27				5	0.62	1	25
28	S^{+6}	$BaSO_4$	2-06-78	6	75.2	512	1
29			2-16-78	4	8.66	59	5
30				4	2.38	16	3
31				3	0.28	2	8
32	Cr^{+3}	Cr_2O_3	3-02-78	5	43.7	64	1
33			3-07-78	3	13.7	20	2
34				4	1.41	2	3
35	S^{-2}	PbS	4-06-78	4	6.21	46	2

(continued)

TABLE 5 (CONTINUED)

Set No.	Element/ Valence State	Compound	Date Generated	Mass Concentration*			
				N	MZ	MT	CV
36				4	5.30	38	2
37				4	1.01	8	3
38				4	0.094	1	4
39			4-10-78	4	14.8	110	2
40				4	65.7	490	2
42	V^{+4}	V_2O_4	4-28-78	4	3.65	6	10
43			5-03-78	4	36.2	59	4
44				4	0.10	<1	60
45			5-08-78	4	9.39	15	10
46				4	1.75	3	2
54	S^{+4}	$La_2(SO_3)_3$		4	16.6	72	1
55				4	13.2	57	1
56				4	3.1	13	6
57				4	0.49	2	1

* N = Number of samples analyzed
MZ = Mass concentration (mean) of valence state element ($\mu g/cm^2$)
MT = Total mass concentration (mean)($\mu g/cm^2$)
CV = Coefficient of variation (percent)

TABLE 6. MASS LOADINGS OF MULTIPHASE VALENCY STATE STANDARDS

Set No.	Element/ Valence State	Compounds	Date Generated	N	Mass Concentration* MZ1	MZ2	CV1	CV2	MT
47	Cr^{+3}, Cr^{+6}	Cr_2O_3, $PbCrO_4$	5-19-78	4	73.7	15.8	2.6	3.9	201
48				4	47.5	9.92	4.5	1.1	128
49				4	7.93	2.04	8.3	1.5	34
50				4	1.05	0.37	16.4	1.6	4
51				4	12.8	18.9	20.0	2.4	131
52				4	1.50	3.77	13.5	1.7	25
53				4	0.35	0.57	7.9	2.8	4
58	V°, V^{+5}	V, V_2O_5		2,2	~0	39.3	1.7	6.8	70
59				2,2	2.2	13.0	1.3	4.3	25
60				2,2	0.68	1.0	12.3	5.0	3
61	S^{-2}, S^{+6}	PbS, $BaSO_4$		2,2	15.2	8.8	0.4	0	173
62				2,2	2.8	1.6	0	4.3	32
63				2,2	0.5	0.2	0.5	0	5

* N = Number of samples analyzed
MZ1, MZ2 = Mass concentration (mean) of valence state elements ($\mu g/cm^2$)
CV1, CV2 = Coefficient of variation for elements 1 and 2 (percent)
MT = Total mass concentration (mean) ($\mu g/cm^2$)

corresponding to about 300 μg, is about two percent. This is insignificant with respect to x-ray scattering (background). Several additional filters were similarly processed, but were fastened to mylar washers, and were subsequently used for characterization of the deposit and for stability measurements.

Deposit Characterization

Moderate to high concentration samples of each single phase valence state were analyzed by x-ray diffraction and fluorescence within a period of two to four months after preparation for comparison to the original powders. The major purpose of this analysis was to identify the presence of phase transformation. The results are presented in Table 7. The x-ray diffraction traces were identical to those of the starting compound, with no evidence for a phase change in any of the standards. The low levels of contaminant elements observed in some of the samples is attributed to some carryover from prior runs in the dust generation apparatus. The levels are low, however, and should have no adverse influence on the standards.

Portions of more lightly loaded filters (1-10 $\mu g/cm^2$ valence/element) were prepared for examination by scanning electron microscopy by coating with a thin layer of gold. Preliminary studies were carried out to evaluate the uniformity of the deposit on the filter and reproducibility among filters for the same run. Samples for the S^{-2} and V^{+4} valence states were examined to evaluate particle distribution as a function of:

- central vs. peripheral location on filters
- replicate filters
- very light ($\sim$0.1 $\mu g/cm^2$) and light ($\sim$1 $\mu g/cm^2$) loadings

Photographs for each condition were taken at about 2000 and 5000 magnifications, and also at about 500 magnifications for lightly loaded samples. A comparison of photographs indicated samples from various locations on the filter and from replicate filters were equivalent.

Subsequently, light and moderately heavy filter loadings of all generated compound standards were examined by the SEM, with photographs taken at about 2000, 10,000 and sometimes 500 magnifications. Particle size analysis was carried out on selected SEM photographs using a Ladd digitizer. Particle distributions were observed to be uniform in all cases, with particle sizes ranging from about 0.2 to 3 or 4 μm. The data is summarized in Table 8. It should be noted that the mass concentration calculated from the number and average size of particles agrees quite well with the measured results, further verifying the uniformity of the deposit. Representative scanning electron micrographs of the various single standards are given in Figures 1 through 3.

Sample Stability

Preliminary experiments were conducted early in the program in which filter samples of six standards having heavy mass loadings ($\sim$50 $\mu g/cm^2$) were subjected to x-ray irradiation. The samples represented the following

TABLE 7. COMPARISON OF GENERATED FILTER STANDARDS TO STARTING COMPOUNDS

Compound	Additional Phases* (X-Ray Diffraction)	Additional Elements* (X-Ray Fluorescence)
S	nc	nc
PbS	nc	Ba, S
$La_2(SO_3)_3$	nc	nc
$BaSO_4$	nc	nc
V	nc	nc
V_2O_4	nc	Pb, Ba, S
V_2O_5	nc	nc
Cr_2O_3	nc	Ba, S
$PbCrO_4$	nc	nc

*nc - no change from starting compound

TABLE 8. MICROSCOPIC EVALUATION OF FILTER STANDARDS*

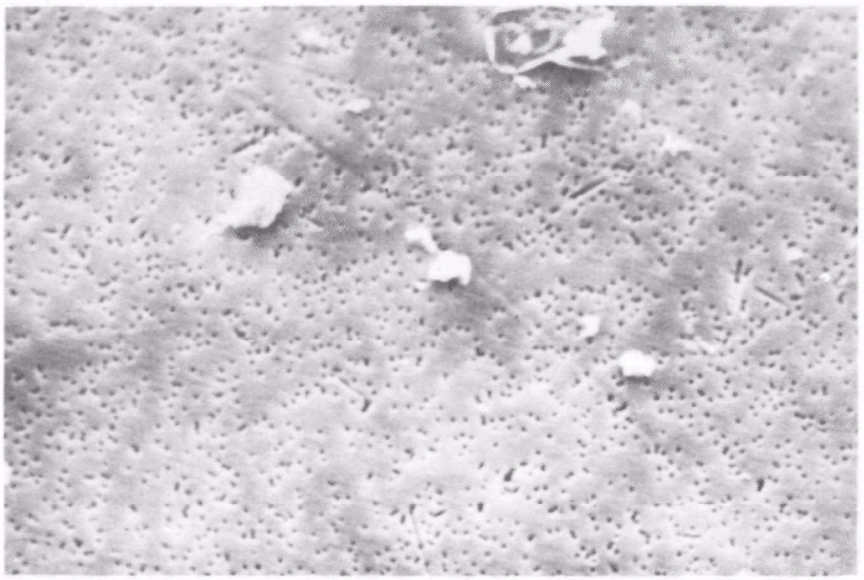
Valence	Compound	Sample No.	Magnification	n	$\bar{d}_o$	MZ_o	MZ
S°	S	9-8	2,200	36	1.28	4.4	9.5
S^{-2}	PbS	37-5	11,000	143	0.28	2.2	1.0
S^{+4}	$La_2(SO_3)_3$	57-6A	2,200	63	1.92	3.2	0.5
S^{+6}	$BaSO_4$	30-2	11,000	104	0.23	0.6	2.4
V	V	25-1	2,200	31	1.58	20.5	37.8
V^{+4}	V_2O_4	45-2	2,200	161	0.79	6.0	9.4
V^{+5}	V_2O_5	13-5A	2,200	69	0.98	1.0	0.9
Cr^{+3}	Cr_2O_3	33-1	2,200	34	1.98	26.5	13.7
Cr^{+4}	$PbCrO_4$	16-5A	11,000	46	0.45	1.0	4.0

* N = number of particles counted

$\bar{d}_o$ = average Martins diameter for particles counted

MZ_o = mass concentration of valence element ($\mu g/cm^2$) estimated by electron microscopy

MZ = actual mass concentration of valence element ($\mu g/cm^2$)



3389-4

(a)

3350-5

(b)

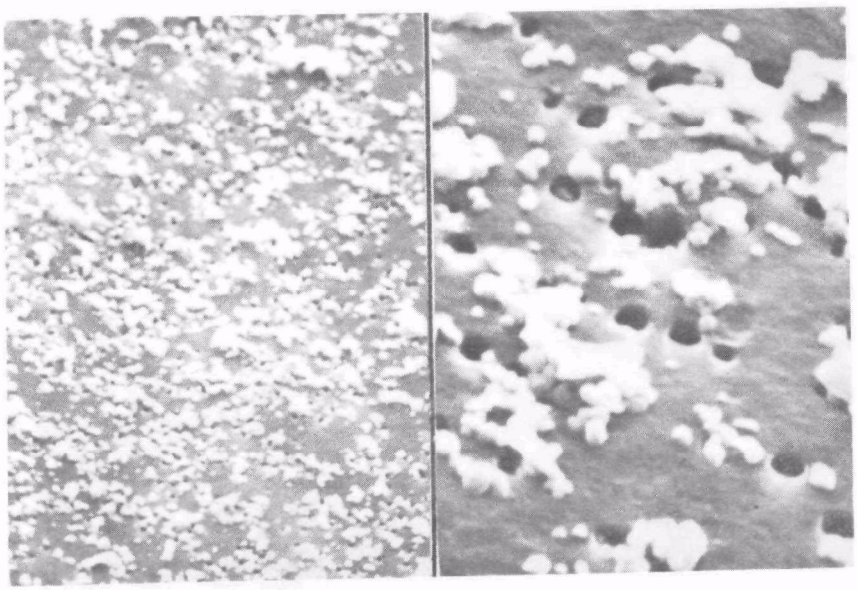
Figure 1 Scanning Electron Micrographs of Sulfur Valence State Standards:

a) S° - Sulfur, 9-8, 9.5µg/cm^2, 3000X

b) S^{-2} - PbS, 37-5, 1.0µg/cm^2, 3000X

3413-5

(c)



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(d)

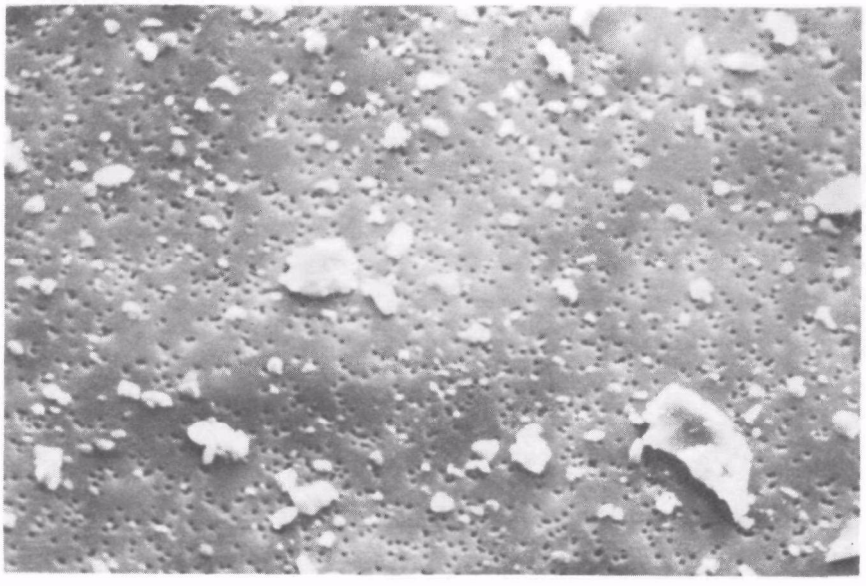
Figure 1 (Continued) Scanning Electron Micrographs of Sulfur Valence State Standards:

c) S^{+4} - $La_2(SO_3)_3$, 57-6A, 0.5µg/cm^2, 3000X

d) S^{+6} - $BaSO_4$, 30-2, 2.4µg/cm^2, Left - 3000X, Right - 15,000X

3390-2

(a)



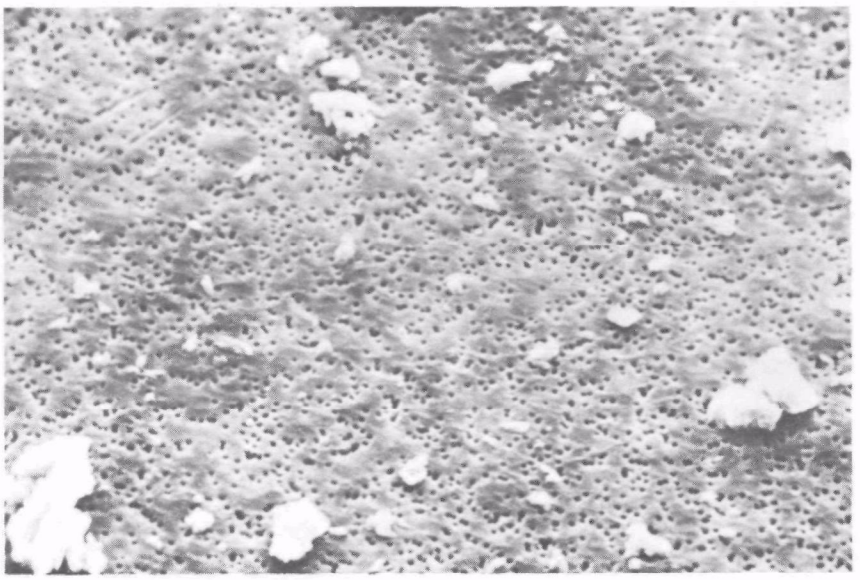
3395-1

(b)

Figure 2 Scanning Electron Micrographs of Vanadium Valence State Standards:

a) V° - Vanadium, 25-1, 37.8µg/cm^2, 3000X

b) V^{+4} - V_2O_4, 45-2, 9.4µg/cm^2, 3000X



3351-1

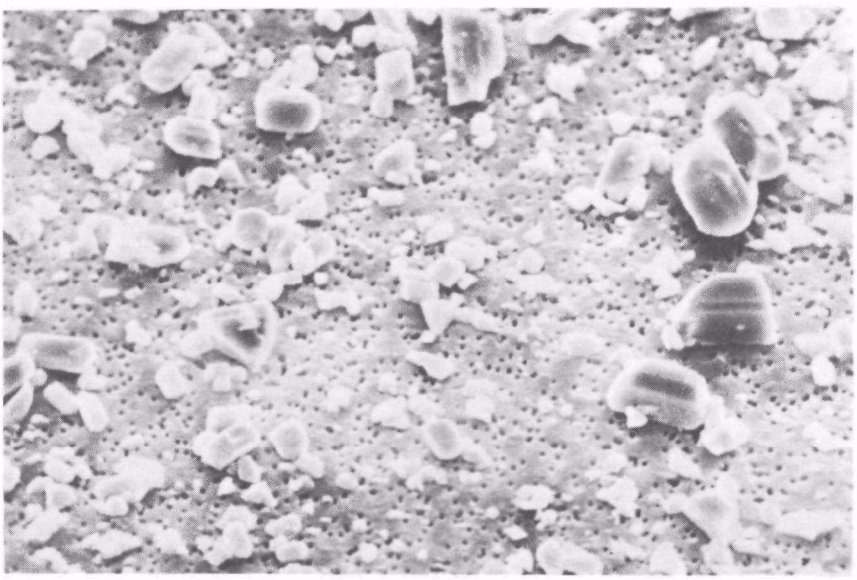
(c)

Figure 2 (Continued) Scanning Electron Micrographs of Vanadium Valence State Standards:

c) V^{+5} - V_2O_5, 13-5A, 0.9µg/cm^2, 3000X

3393-2

(a)



3356-3

(b)

Figure 3 Scanning Electron Micrographs of Chromium Valence State Standards:

a) Cr^{+3} - Cr_2O_3, 33-1, 13.7µg/cm^2, 3000X

b) Cr^{+6} - $PbCrO_4$, 16-5A, 4.0µg/cm^2, 3000X

oxidation states: S°, S^{+6}, V°, V^{+5}, Cr^{+3}, Cr^{+6}. Initially, uncoated samples were subjected to x-ray exposures represented by a chromium target tube operated at 45 KV and 25 ma, with the sample in vacuum. After 23 hours, the S standard (9-8A) burned through at the center. The $BaSO_4$ and a duplicate S sample were carbon coated and re-exposed. The $BaSO_4$-carbon coated sample survived a 100 hour exposure, but with an apparent reduction in S intensity by about 40 percent. The replicate S standard showed a 3-fold reduction in S intensity after carbon coating. This sample also failed after approximately 20 hours x-ray exposure.

The failure of these samples was attributed to embrittlement of the substrate filter and eventual fracture due to stresses during sample loading and unloading. The loss in intensity after exposure was felt to be the result of sample loss during handling, as these initial evaluation samples were not coated with nitrocellulose.

After all the single phase standards were generated, samples representing moderate to heavy concentrations for each of the single state standards were treated with parlodian, attached to mylar washers and trimmed to 25 mm diameters. These samples were treated according to the following schedule for 10 days:

16 hours/day	-	ultraviolet irradiation in closed containers
8 hours/day	-	sunlight (window) exposure in laboratory air
0.5 hours/day	-	held in vacuum
0.5 hours/day	-	irradiated by 45 KV - 25 ma x-rays (chromium target tube) in vacuum

These evaluation samples were examined each day for evidence of degradation. Also, x-ray intensities of the elements of interest were measured at the start and end of the exposure schedule. After several days, the samples assumed a saddle-shape due to annealing of the polycarbonate substrate and insufficient resistance by the mylar washer. Therefore, final x-ray intensities were more variable than would generally be expected. The standard samples mounted in the EPA holders (described in the next section) will not suffer this warping problem. The only noted degradation was an embrittlement of the polycarbonate substrates, resulting in very fragile samples. In two cases, attempts to flatten the samples prior to x-ray intensity measurements resulted in the samples breaking. An identification of the samples and results are given in Table 9.

No deterioration (during the 10-day test period) was noted for exposure to laboratory air, ultraviolet radiation or vacuum exposure. The relative changes in x-ray intensity after a cumulative 5-hour x-ray irradiation are probably due to sample distortion. There was no evidence for sample loss or transformation (phase change) as a result of the stability evaluation.

As the elemental sulfur standard was broken during these tests, a duplicate (coated) standard was subjected to an 8-hour x-ray exposure. X-ray intensity of the sulfur K_{α} line (PET analyzing crystal) agreed to initial intensity

TABLE 9. SAMPLES USED FOR X-RAY STABILITY EXPERIMENTS

Valence	Component	Sample No.	Mass Concentration ($\mu g/cm^2$)	X-Ray Intensity - (cps)		
				Initial	Final*	Change (%)
S°	S	9-6	54.0	4.3	-	-
S^{-2}	PbS	40-2A	229	8.6	7.5	-13
S^{+4}	$La_2(SO_3)_3$	54-1A	57.8	22.6	17.5	-22
S^{+6}	$BaSO_4$	28-1	75.2	15.1	15.9	+5
V°	V	25-1A	132	1.8	2.0	+11
V^{+4}	V_2O_4	43-1A	126	6.4	3.6	-44
V^{+5}	V_2O_5	10-1	75.8	4.6	-	-
Cr^{+3}	Cr_2O_3	32-4	43.7	3.1	7.5	+143
Cr^{+6}	$PbCrO_4$	18-5	59.6	13.6	18.4	+35

* Blank values represent samples that were broken during attempt to flatten to original geometry.

within 4 percent. It is concluded that there are no evaporative losses of elemental sulfur from coated filters in the level of vacuum employed in x-ray spectrometers.

IDENTIFICATION OF STANDARDS

The identification of standards by valence state and mass concentration of the valence/state element is given in Table 10. Total mass concentrations and an inventory of replicate samples available for use as standards is also given.

TABLE 10. SAMPLE INVENTORY

Valence State	Compound	Set	Mass Concentration-$\mu g/cm^2$		Samples*
			Valence Element	Total	
S°	S	9c	0.69	0.69	3
		9b	9.5	9.5	3
		9a	54.0	54.0	0
S^{-2}	PbS	38	0.09	0.67	4
		37	1.01	7.5	2
		36	5.30	39.5	4
		35	6.21	46.3	4
		39	14.8	110	3
		40	65.7	490	4
S^{+4}	$La_2(SO_3)_3$	57	0.49	2.6	4
		56	3.1	16.7	4
		55	13.2	71	4
		54	16.6	89	4
S^{+6}	$BaSO_4$	31	0.28	2.0	4
		30	2.38	17.3	4
		29	8.66	63	4
		28	75.2	547	4
V°	V	27	0.62	0.62	4
		22	1.13	1.1	4
		26	7.87	7.9	4
		21	17.5	17.5	4
		20	25.6	25.6	2
		24	32.3	32.3	3
		25	37.8	37.8	1
V^{+4}	V_2O_4	44	0.10	0.16	2
		46	1.75	2.9	4
		42	3.65	5.9	4

(continued)

TABLE 10. (continued)

Valence State	Compound	Set	Mass Concentration-μg/cm^2		Samples*
			Valence Element	Total	
		45	9.39	15.1	3
		43	36.2	59	4
V^{+5}	V_2O_5	13	0.92	1.6	3
		12	6.56	11.7	3
		11	42.2	75	2
		10	75.8	135	3
Cr^{+3}	Cr_2O_3	34	1.41	2.1	4
		33	13.7	20.0	3
		32	43.7	64	2
Cr^{+6}	$PbCrO_4$	17	0.46	2.9	4
		16	4.01	24.9	3
		15	27.6	172	2
		18	59.6	370	3
S^{-2}, S^{+6}	$PbS, BaSO_4$	63	0.2, 0.5	4.9	4
		62	1.6, 2.8	30.9	4
		61	8.8, 15.2	168.7	4
V°, V^{+5}	V, V_2O_5	60	0.68, 1.0	2.5	4
		59	2.2, 13.0	25.4	4
		58	∿0, 39.3	70.2	4
Cr^{+3},Cr^{+6}	Cr_2O_3,$PbCrO_4$	53	0.35, 0.57	3.9	4
		52	1.50, 3.77	24.5	4
		51	12.8, 18.9	130.5	3
		50	1.05, 0.37	3.7	4
		49	7.39, 2.04	22.9	4
		48	47.5, 9.92	128.1	4
		47	73.7, 15.8	201.2	4

* Number of 47mm diameter filters (not treated with parlodian) in addition to the duplicate set of standards.

APPENDIX A

SAMPLE GENERATION APPARATUS (FRED)

"FRED" is an apparatus constructed at ADL to generate test atmospheres containing dust for occupational hygiene studies. The device, which is shown in Figure A.1, consists of a Wright Dust Feeder, an aerosol charge neutralizer, and an 80-liter stainless steel dust chamber.

Dust samples to be dispersed in the apparatus are compressed into a special holder which is attached to the Wright Dust Feeder. In operation, the holder (and the compacted dust) is slowly rotated and driven against a stationary scraper blade which continuously removes dust from the compacted surface at a uniform rate. Compressed air entering the container entrains and removes the dust particles. Both the compressed air flow and the dust holder advance rate may be varied to provide a wide range of dust concentration. There is also an auxiliary port for introducing additional compressed air for further dilution. Dust output may be estimated from knowledge of the compact advance rate, compact density, and air flow rate.

Dust particles may accumulate electrical charge in the dispersal process; consequently, the dispersed dust is passed through a charge neutralizer (Thermo-Systems Model 3054) before it is introduced into the dust chamber. The neutralizer is a 10-millicure krypton-85 beta source. Beta rays interact with air molecules to generate both positive and negative ions. The ions become attached to the dust particles of opposite charge.

The dust chamber was constructed from two stainless steel stock pots. The pots are held together by three latches with a soft rubber gasket seal between the pots. The system is operated at a positive pressure with respect to the atmosphere. Effluent aerosol from the dust chamber is vented to a hood.

There are 12 ports on the dust chamber for extracting samples. Twelve filter holders may be mounted inside the chamber, as is shown in Figure A-2. Flow rate through the samplers is controlled by 12 critical orifices. The orifices are mounted on the U-shaped vacuum line shown in Figure A-1.

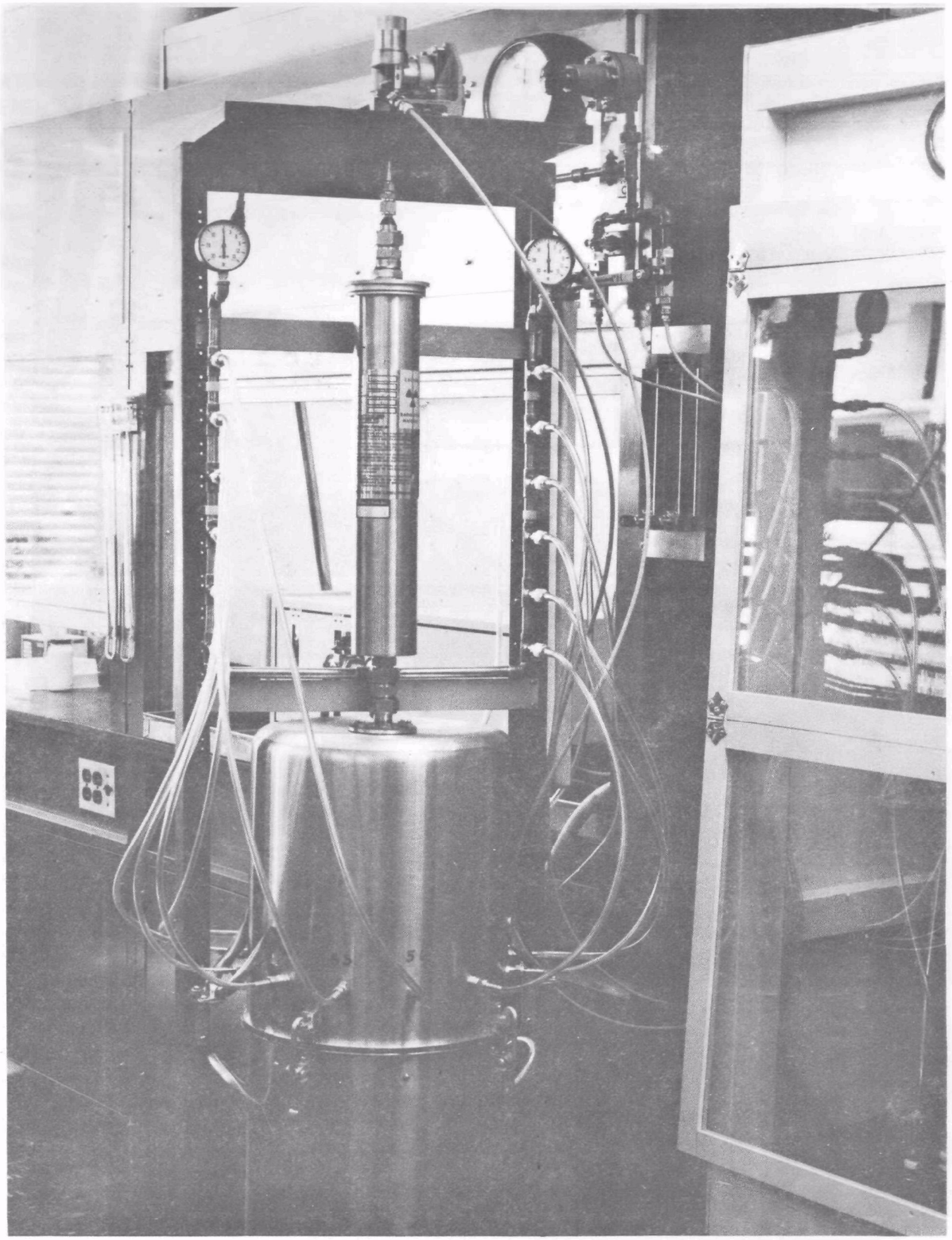


Figure A-1. FRED dust generation system.

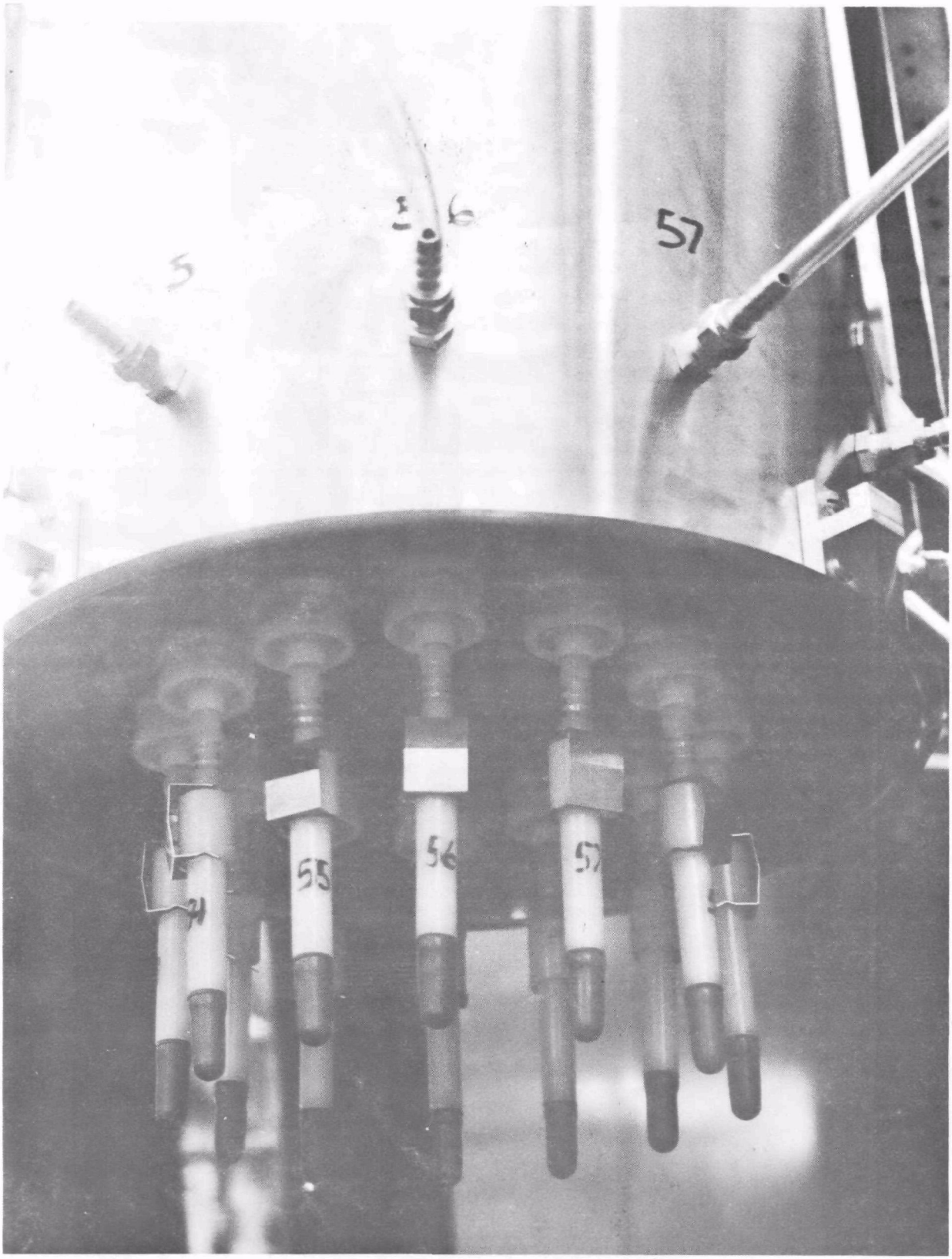


Figure A-2. Cyclones & filter holders.

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(Please read Instructions on the reverse before completing)

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16. ABSTRACT

The preparation and characterization of standard samples representing several valence states for sulfur, vanadium, and chromium are described. The standards will be used by the U.S. Environmental Protection Agency to investigate the potential for determining valence state by high resolution wavelength dispersive x-ray emission analysis. A total of 40 single state and 13 multistate standards were prepared by dust generation and collection on polycarbonate filters. The prepared samples and valence states include sulfur (0, +4, +6, -2), vanadium (0, +4, +5), and chromium (+3, +6). At least three standards were prepared for each valence state, with mass concentration of the valence state element in the range 1 to 50 $\mu g/cm^2$. The prepared samples were coated with a thin layer of nitrocellulose by a wicking procedure to provide a protective coating and to prevent loss of material. Representative samples were analyzed for the uniformity of the deposit, mean particle size and stability in air, and x-ray irradiation.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
* Standards * Sulfur * Vanadium * Chromium * Valence X-ray fluorescence		07B 06E 20F

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