

ALUMINUM OXIDE IN WORKPLACE ATMOSPHERES



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Method no.: ID-109-SG

Method Classification:

OSHA Standard: 15 mg/m<sup>3</sup> (Total Dust) (Ref. 11.1)  
5 mg/m<sup>3</sup> (Respirable Fraction) (Ref. 11.1)

Sampling Procedure: Collection medium - 5 µm LAPVC filters  
Sampling rate - 2.0 L/min  
Recommended air volume - 100-960 L

Analytical Procedure: Sample filters are fused with a flux consisting of LiBO<sub>2</sub>, NH<sub>4</sub>NO<sub>3</sub> and NaBr in platinum crucibles. The fused sample is then put into aqueous solution and analyzed for aluminum by flame atomic absorption.

Detection Limit: 0.5 µg/mL

Precision: The average recovery for this analysis is 96% and the standard deviation is ±9%.

Status of Method: Partially Validated

Date Approved:  
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## 1. General Discussion

- 1.1 The sample is collected on a LAPVC - 5- $\mu\text{m}$  membrane filter.
- 1.2 The sample filters are fused with  $\text{LiBO}_2$ ,  $\text{NH}_4\text{NO}_3$  and  $\text{NaBr}$  in platinum crucibles.
- 1.3 The fused sample is dissolved in a warm aqueous solution containing  $\text{K}^+$  and  $\text{HNO}_3$  and  $\text{HCl}$  and diluted to volume with deionized water.
- 1.4 The sample solution is then analyzed for aluminum by atomic absorption using the "General Metals Procedure" (Method ID-121) (Ref. 11.2).

## 2. Range and Detection Limit

- 2.1 The upper limit of sample analysis is based on the upper limit of linearity of the atomic absorption analysis of aluminum which is 50  $\mu\text{g}/\text{mL}$  (50 ppm) (Ref. 11.3).
- 2.2 The lower limit of sample analysis is based on the detection limit of 0.05  $\mu\text{g}/\text{mL}$ . For a 100 mL sample volume and a 100 L air volume the lower limit is 0.05  $\text{mg}/\text{m}^3$ .

## 3. Precision and Accuracy

- 3.1 Data on a batch of eight samples run at the OSHA Analytical Laboratory indicate an average recovery of greater than 96%, with a approximate standard deviation of  $\pm 9\%$  on samples containing between 0.2 and 10  $\text{mg}$  of  $\text{Al}_2\text{O}_3$ .
- 3.2 Factors which may influence precision and accuracy are possible losses occurring during fusion and matrix effects during atomic absorption analysis.

## 4. Advantages and Disadvantages

- 4.1 The fusion method of sample preparation is not as convenient as the acid digestion workup used for aluminum analysis but is necessary because aluminum oxide is not completely dissolved using the acid digestion.
- 4.2 The major advantage of the fusion method is its accuracy. Tests using aluminum oxide standards have shown that the fusion method is superior in accuracy to the acid digestion method which gives low results.
- 4.3 While weighed-out anhydrous aluminum oxide can be used as a standard of quality control, it is more convenient and just as accurate to carry soluble aluminum Quality Control samples through the fusion method.
- 4.4 Interferences are the same as those found in the atomic absorption analysis of aluminum. Ionization interferences are controlled by making the sample solution 1000 ppm in potassium ion.

## 5. Apparatus

- 5.1 Two- or three-piece filter cassette holders with LAPVC - 5- $\mu\text{m}$  membrane filters
- 5.2 Personal sampling pump capable of being calibrated at various flow rates between 1.0 and 2.0 Lpm
- 5.3 Platinum crucibles and platinum-tipped crucible holders
- 5.4 Meker burner
- 5.5 Ceramic triangles

- 5.6 125 mL Phillips beakers
  - 5.7 50 mL volumetric flasks
  - 5.8 Hot plate
  - 5.9 Atomic absorption spectrophotometer with burner head and attachments for nitrous oxide-acetylene flame.
6. Reagents.- All reagents should be ACS reagent grade or better.
- 6.1 HNO<sub>3</sub>, concentrated
  - 6.2 HCl, concentrated
  - 6.3 Anhydrous aluminum oxide to prepare a 1000 ppm Al solution, or a certified commercially prepared aqueous 1000 ppm Al stock standard.  
  
Note: Chromatographic grades of aluminum oxide (acidic, basic or neutral washed alumina) should not be used for preparation of standards.
  - 6.4 5000 ppm KCl solution - Prepare by adding 19.1 g KCl and diluting to 2 L with deionized water.
  - 6.5 Prepare flux as a 20:4:1-by-weight mixture of LiBO<sub>2</sub> and NH<sub>4</sub>NO<sub>3</sub>, and NaBr. The flux must be well mixed. If chunks or large crystals are present, the flux should be ground in a mortar. Keep flux in a tightly stoppered brown bottle. Flux begins a slow decomposition after mixing (ammonia is evolved) and should not be used more than six months after preparation.
7. OSHA Collection Procedure
- 7.1 A known volume of air is drawn through a tared LAPVC 5-μm pore size filter (e.g., FWS-B).
  - 7.2 The minimum recommended air volume is 100 L.
  - 7.3 The maximum recommended air volume is 960 L and the maximum recommended flow rate is 2.0 L/min (Ref. 11.4).
  - 7.4 After sampling, the filter is weighed.
  - 7.5 Sample submission to the analytical laboratory requires a sample weight sufficient to indicate a violation (Ref. 11.5).
  - 7.6 Sample cassettes are plugged, sealed with Form OSHA-21 seals and sent to the analytical laboratory.
  - 7.7 Samples are stable indefinitely in storage.
  - 7.8 Bulk samples may also be sent in for analysis.

## 8. Standard Preparation

- 8.1 Working standards may be prepared from a 1000 ppm Al stock solution by diluting to the appropriate concentrations. The working standards should range from 0.5 ppm to 100 ppm. See Table I for dilution scheme.
- 8.2 The standards should be prepared so that the final matrix matches that of the samples. The amount of flux added to a sample which will have a final solution volume of 50 mL is 0.5 g, or 1% w/v. Therefore, a 2% solution of blank flux (no aluminum) for use in making standards may be prepared as follows:

Place 20 g of flux in a large beaker. Add about 500 mL of deionized water, 10 mL of concentrated  $\text{HNO}_3$  and 20 mL of concentrated HCl. Place the beaker on a hotplate and heat until all the flux has dissolved. When the solution has cooled, transfer the solution to a 1000 mL volumetric flask and dilute to volume with deionized water.

## 9. Analytical Procedure

- 9.1 Phillips beakers should be washed by refluxing with conc. nitric acid, cooling and rinsing with deionized water. Volumetric flasks should be rinsed with 10% nitric acid and thoroughly rinsed with deionized water.

- 9.2 Platinum crucibles are cleaned as follows:

Remove any solids sticking to the inside of the crucible by rubbing with a plastic or wood object (metallic objects can scratch).

Rub the inside of the crucible with a dampened Kim-Wipe coated with Type 1 government cleanser. Some black, finely-divided platinum metal may come off but the amount is insignificant. Rinse out all traces of cleanser with deionized water.

Add 1-2 mL of conc. nitric acid to the crucible and, holding the crucible about 1/4 inch below its top with platinum-tipped crucible tongs, heat the crucible over the Meker burner flame until the nitric acid boils and yellow fumes come off. Again rinse the crucible with deionized water.

Flame the empty crucible over the Meker burner flame until it glows a dull orange-pink color. Never heat to white-hot as the metal will melt and develop cracks around crystals when recooling. The best flame for use in this procedure (and for fusing samples) is obtained by opening the oxygen control windows on the burner all the way and adjusting the fuel control valve on the bottom to give a flame with a blue cone extending about 1/4 inch above the top of the burner. The crucible should be held just above the blue cone. Always place hot crucibles on ceramic triangles to cool.

- 9.3 Carefully remove the filter from the cassette and fold into quarters. Place the filter in the crucible.
- 9.4 Moisten the surface of the packet with several drops (0.4-0.8 mL) of deionized water to help it hold its shape. It is necessary that mixed cellulose ester filters (e.g., AA filters used in aluminum Quality Control samples) be well moistened to prevent them from rapidly bursting into flame upon heating, since this rapid burning scatters the crucible contents.
- 9.5 Cover the moistened filter with approximately 0.5 g of flux. Record the sample and crucible numbers for each sample.
- 9.6 Slowly and carefully warm the crucible as the filter begins to decompose. After the filter has decomposed completely, the crucible can be rapidly heated to an orange-pink glow. Swirl the molten flux around to dissolve any material sticking to the sides of the crucible. Heat until all the material has been dissolved (except for some ash which may remain in the bottom).

- 9.7 While still hot, pour the molten sample quickly into a 125 mL Phillips beaker containing 10 mL of 5000 ppm potassium ion solution, 0.5 mL conc. HNO<sub>3</sub>, 1 mL conc. HCl and approximately 25 mL of deionized water. As the drop enters the solution, it fractures into small fragments. Do not let the flux harden in the crucible. If a small drop sticks to the lip of the crucible, chip it off as soon as it hardens and add it to the beaker.
- 9.8 Heat the Phillips beaker contents on a hotplate until all of the fused sample fragments dissolve. A watch glass can be placed over the beaker mouth to prevent excessive liquid loss. Small amounts of black filter paper ash may be present in the final solution, which can be filtered if necessary.
- 9.9 Cool and transfer the Phillips beaker contents to a 50 mL volumetric flask and dilute to volume with deionized water. If the sample represents a small air volume (~100 L), use a smaller volumetric flask and proportionally smaller amounts of solutions in the Phillips beaker.
- 9.10 The samples and standards are then analyzed for aluminum using atomic absorption spectrophotometry. (Ref.11.2)
- 9.11 Soluble aluminum Quality Control samples should be prepared and analyzed the same way as air samples, except that the final solution volume should be 25 mL.
- 9.12 Bulk sample materials may be weighed onto a filter or directly into a tared crucible and prepared and analyzed in the same way as an air sample. The maximum recommended weight for a bulk sample is 200 mg.

## 10. Calculations

- 10.1 A linear regression of standard peak height or absorbance vs. µg, of aluminum is performed using the OSHA Auto AA Program. The sample results are calculated based on sample absorbance values.

$$\text{Al}_2\text{O}_3 \frac{\text{mg}}{\text{m}^3} = \frac{(\text{mg/mL Al}^*)(\text{sample volume (mL)})(\text{dilution factor})(\text{G.F.})}{\text{Air Volume (L)}}$$

\*Blank corrected  
G.F.=Gravimetric factor = 1.8894

- 10.2 Wipe sample values are reported as total milligrams. Bulk sample values are reported as a percentage of the sample weighed out.

## 11. References

- 11.1 Code of Federal Regulations, Title 29, 1910.1000, Table Z-1, U.S. Office of the Federal Register National Archives and Records Administration, Washington, DC, 2000.
- 11.2 OSHA Manual of Analytical Methods, unpublished.
- 11.3 Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer Corp., 1975.
- 11.4 OSHA Sampling and Analytical Techniques Table, Industrial Hygienists Field Operations Manual, OSHA Instruction CPL 2-2.20, Apr.2, 1979).
- 11.5 Letter from D. E. MacKenzie, Office of Field Coordination, OSHA Instruction CPL 2-2.25, May 8, 1979, page 3.

TABLE I - STANDARD PREPARATION

Working standard	Stock soln. used	mL stock used	Final vol. mL
100 ppm	1000 ppm	10	100
50 ppm	1000 ppm	5	100
20 ppm	1000 ppm	2	100
10 ppm	1000 ppm	1	100
5 ppm	100 ppm	5	100
2 ppm	100 ppm	2	100
1 ppm	100 ppm	1	100
0.5 ppm	10 ppm	5	100

Fifty mL of the 2% flux solution and 20 mL of the 5000 ppm K<sup>+</sup> solution are added to the 100 mL volumetrics before the solutions are diluted to volume.

#### APPENDIX I Back-up Data

##### 1. Recovery of Aluminum Oxide Using the Fusion Technique and Atomic Absorption Analysis

Eight aliquots of Al<sub>2</sub>O<sub>3</sub> were weighed out and fused in platinum crucibles using the technique described in the Aluminum Oxide Procedure. The fused samples were then placed in Phillips beakers, each containing 0.5 mL conc. HNO<sub>3</sub>, 20 mL of 5000 ppm KCl solution about 50 mL of deionized water.

The beakers were heated to dissolve the solid material, then cooled. The cooled samples were transferred to 50 mL volumetrics and diluted to volume with deionized water. The samples were then analyzed by atomic absorption, using aqueous aluminum standards. The recovery data appear in the table below.

Table 1 - Recovery of Al<sub>2</sub>O<sub>3</sub>

Sample #	Ave mg Al <sub>2</sub> O <sub>3</sub>	Theor mg	Recovery
AL1	6.11	6.36	0.9607
AL2	1.37	1.40	0.9786
AL3	8.28	9.03	0.9169
AL4	4.42	4.60	0.9609
AL5	0.276	0.270	1.0222
AL6	1.95	2.05	0.9512
AL7	0.610	0.628	0.9713
AL8	3.05	3.23	0.9493

For the above data, the average recovery was 0.9633.

##### 2. Recovery of Aluminum Oxide Using Standards Containing the Flux Material Used in the Fusion of the Al<sub>2</sub>O<sub>3</sub> Samples

Since matrix effects are sometimes significant in atomic absorption analysis, a recovery study was done to test the effect of the flux matrix on the recovery of Al<sub>2</sub>O<sub>3</sub>. Previously, samples which had been fused with the flux material described in the Aluminum Oxide Procedure had been analyzed by AA using aqueous Al standards which did not contain any flux. The purpose of the study was to compare the recoveries of spiked samples analyzed using the aqueous Al standards with the recoveries of the same samples analyzed using flux-containing standards.

Eighteen aluminum samples, six at each PEL level, and eight Al standards (ranging from 0.5 to 100 ppm) were prepared in such a way as to duplicate the matrix of fusion samples as closely as possible. The 18 samples were then analyzed first using the aqueous Al standards, then again using the flux-containing standards. The results appear in Table 2 and Table 3.

Table 2

Sample #	PEL level	Aqueous Standards			Flux Standards		
		µg found	µg theor	recovery	µg found	µg theor	recovery
1/2x1	1/2	911.4	1000	0.911	1045.8	1000	1.046
1/2x2		871.6	1000	0.871	980.3	1000	0.980
1/2x3		915.0	1000	0.915	1054.0	1000	1.054
1/2x4		900.5	1000	0.900	1029.4	1000	1.029
1/2x5		951.2	1000	0.951	1021.2	1000	1.021
1/2x6		878.8	1000	0.879	1029.4	1000	1.029
1x1	1	2279.0	2500	0.912	2577.2	2500	1.031
1x2		-	-	-	2484.2	2500	0.994
1x3		2225.9	2500	0.890	2614.7	2500	1.046
1x4		2274.9	2500	0.910	2690.1	2500	1.076
1x5		2217.8	2500	0.887	2577.2	2500	1.031
1x6		2250.4	2500	0.900	2364.1	2500	0.946
2x1	2	4456.5	5000	0.981	4757.8	5000	0.952
2x2		4466.9	5000	0.893	4717.9	5000	0.944
2x3		4405.1	5000	0.881	4757.8	5000	0.952
2x4		4466.9	5000	0.893	4828.1	5000	0.966
2x5		4384.6	5000	0.877	4781.2	5000	0.956
2x6		4394.8	5000	0.879	4839.8	5000	0.968

Table 3 - Recovery Data

Standard	PEL Level	Ave Recovery	SD	CV
Aqueous	1/2	0.905	0.0284	0.0314
	1	0.900	0.0113	0.0126
	2	0.886	0.0236	0.0084
AMR = 0.987 Flux	S <sub>pooled</sub>	0.0186	CV <sub>pooled</sub>	0.0206
	1/2	1.026	0.0259	0.0252
	1	1.021	0.0452	0.0443
	2	0.956	0.0092	0.0096
AMR = 1.001	S <sub>pooled</sub>	0.305	CV <sub>pooled</sub>	0.0299

### 3. Addition of HCl to Samples and Standards to Help Dissolve the Flux

It is considerably more convenient, when preparing standards, to prepare a solution of flux to be added to the standard solution, rather than adding solid flux mixture. However, the amount of flux mixture needed to make up a 2% solution is difficult to dissolve in just nitric acid alone. Therefore, a 1-mL aliquot of HCl was added to a test mixture of 1 g flux, 0.5 mL HNO<sub>3</sub> and about 25mL deionized water. The flux dissolved much more quickly upon heating than with HNO<sub>3</sub> alone.

Four standards were prepared: a 20 ppm and a 2 ppm Al with HNO<sub>3</sub> added, and a 20 ppm Al with HNO<sub>3</sub> only. The two sets of standards were analyzed by atomic absorption and the results were compared. At both levels, the absorbances agreed very well, indicating that the addition of 2% HCl to samples and standards will aid in the dilution of the flux material, but won't adversely affect the analysis.