MASTER

SPECTROGRAPHIC DETECTION OF TRACE ELEMENTS
IN ALUMINUM METAL (U)

O. P. Killeen

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UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

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P. O. Box Y
OAK RIDGE, TENNESSEE 37831

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INTRODUCTION

Characterization of the purity of aluminum metal has necessitated a method for the detection of trace elements in this matrix. Many procedures for the analysis of aluminum have been published⁽¹⁾ but none cover as many elements or offer the necessary sensitivity to satisfy the indicated needs. Further, traditional aluminum spectrography involves spark excitation which would not be readily compatible with the anticipated sample geometry.

ANALYTICAL METHOD

REAGENTS AND EQUIPMENT

Aluminum Metal Rods

Specpure, (a) 6.35 mm diameter.

Argon

Laboratory grade.

Aluminum Oxide

Specpure or equivalent.

Bubble Caps

See Trap, Entrainment.

Comparator

Microphotometer, Jarrell-Ash 21-000.

Developer

Eastman Kodak D-19.

Developing Machine

Nitrogen Burst agitation system, Calumet BW-813, modified for one-gallon tanks.

Dishes, Porcelain

Coors 2, 120-milliliter capacity.

Electrodes, Counter

NCC SP 9009.

Electrodes, Supporting

NCC SP 9019.

(a) Johnson, Matthey and Company.

Fixer

Eastman Kodak Rapid Fixer with hardener.

Flasks

500-milliliter Erlenmeyer, socket joint 35/25.

Graphite

National Carbon Company, Grade SP-2.

Hydrochloric Acid

Reagent grade.

Impurities for Standards

Johnson-Matthey, or other spectrographically pure chemicals.

Mixer/Mill

Spex Industries 8000.

Nitric Acid

Reagent grade.

Oxygen

Laboratory grade.

Pestles, Plastic Ball

Clear plexiglass, 3/8-inch diameter.

Photographic Plates

Eastman Kodak Type SA-1.

Power Source

Special Design, UCNC Drawing EE-46378.

Spectrograph

Jarrell-Ash with Wadsworth mounted grating, reciprocal linear dispersion $2.42 \text{ \AA/mm}$ in the second order.

Stallwood Jet

Water cooled with a quartz dome, Spex Industries 9027 and 9026.

Trap, Entrainment

Sized to fit a 500-milliliter Erlenmeyer flask.

Venting Tool

Size 72 drill inverted in a pin vise.

Watch Glasses

Speedy vap, 4-inch diameter.

Vials, Plastic

Made of polystyrene, $1/2" \times 1"$, $1/2" \times 2"$, $3/4" \times 2"$, and $1 1/4" \times 3"$, with polyethylene caps.

PROCEDURE

Conversion of Aluminum Metal to Aluminum Oxide

1. Place about 0.3 to 0.5 gram of the aluminum shavings sample in a 500-milliliter socket-joint Erlenmeyer flask.
2. Pickle with aqua regia.
3. Wash well with distilled water.
4. Add aqua regia and heat slowly to be sure the reaction starts but does not foam over the flask. Make additions of aqua regia as needed to sustain the reaction.
5. After all the aluminum has dissolved, evaporate to dryness on a hot plate.
6. Add nitric acid to dissolve the residue and quantitatively transfer the resulting solution to a porcelain dish. Evaporate the solution to dryness with nitric acid a total of two times after transferring the solution to the dish.

7. Place the dish in a 200° C muffle. Set the temperature controller at 850° C and allow the muffle to come to 850° C at its own rate. Keep the sample in the muffle for one hour after it reaches 850° C.
8. Allow the sample to cool in a desiccator, then transfer it into a plastic vial with a ball pestle and grind it in the Mixer/Mill for five minutes.

Analysis

1. Weigh 100 milligrams of the aluminum oxide, previously prepared, and 175 milligrams of graphite into a 1/2 by 1-inch plastic vial with a ball pestle.
2. Grind the mixture in the Mixer/Mill for one minute.
3. Weigh 50 milligrams of the mixture into each of three electrodes having 3 1/2 by 8 1/2 millimeter craters (NCC SP 9019). Space evenly four vent holes around the inside walls of the crater.
4. Excite each electrode and develop the resulting plate according to the parameters in Table 1.
5. Compare the spectrum obtained with standard spectra of known concentrations.

PREPARATION OF STANDARDS

1. Weigh each impurity listed in Tables 2 and 3 to prepare the impurity mixtures for Groups I and II.
2. Grind each mixture of the impurities in the Mixer/Mill for five minutes. Ten thousand micrograms of each element weighed are present in these mixtures.
3. Prepare the high standard of Group I and Group II by adding the appropriate impurity mixture to pure aluminum metal. As it is difficult to take a predesignated weight of metal shavings, take approximately one gram, record its exact weight, and calculate the amount of impurity mixture necessary by using the ratios given in Tables 4 and 5.
4. Place the aluminum and impurities in a 500-milliliter Erlenmeyer flask. Cover the contents with concentrated nitric acid and put an entrainment trap over the flask.
5. Add aqua regia dropwise through the trap cap to keep the reaction going.

Table 1
EXCITATION CONDITIONS FOR ALUMINUM

Parameter	
Analytical Gap (mm)	3
Charge (mgs)	50 (includes graphite)
Electrodes	
Counter	1/8" D (pointed)
Supporting	NCC SP 9019
Excitation (DC amp-sec)	16 - 130
Photographic Plates (number and type)	Three - EK SA-1
Plate Processing (20° C)	
EK D-19 Developer (min)	3
EK Rapid Liquid Fixer (min)	1
Useful Camera Range	
1st Order ($\text{\AA}$)	4100 - 4500
2nd Order ($\text{\AA}$)	2300 - 3750
Slit Height (mm)	2
Slit Width (microns)	20
Water-cooled Stallwood Jet	
Argon (l/min)	3
Oxygen (l/min)	1 1/2

Table 2
PREPARATION OF IMPURITY MIXTURE FOR GROUP I STANDARDS

Element	Compound	Factor ⁽¹⁾ (gms)	Factor x 10 ⁻² (2) (gm)
Ag	Ag ₂ O	1.0742	0.0107
B	H ₃ BO ₃	5.7157	0.0572
Be	BeO	2.7752	0.0278
Bi	Bi ₂ O ₃	1.1148	0.0112
Ca	CaCO ₃	2.4973	0.0250
Cd	CdO	1.1423	0.0114
Co	Co ₃ O ₄	1.3620	0.0136
Cr	Cr ₂ O ₃	1.4614	0.0146
Cu	CuO	1.2518	0.0125
Fe	Fe ₂ O ₃	1.4297	0.0143
Ga	Ga ₂ O ₃	1.3442	0.0134
In	In ₂ O ₃	1.2090	0.0121
Mg	MgO	1.6579	0.0166
Mn	Mn ₃ O ₄	1.3883	0.0139
Mo	MoO ₃	1.5003	0.0150
Ni	NiO	1.2725	0.0127
Pb	PbO	1.0772	0.0108
Sb	Sb ₂ O ₄	1.2628	0.0126
Si	SiO ₂	2.1392	0.0214
Sn	SnO ₂	1.2696	0.0127
Ti	TiO ₂	1.6681	0.0167
Tl	Tl ₂ O ₃	1.1174	0.0112
V	V ₂ O ₅	1.7851	0.0179
Y	Y ₂ O ₃	1.2699	0.0127
Zn	ZnO	1.2447	0.0124
Zr	ZrO ₂	1.3508	0.0135
Total			0.4239

(1) Or weight of compound equal to one gram of element.

(2) Amount weighed equal to 0.01 gram of element.

Table 3
PREPARATION OF IMPURITY MIXTURE FOR GROUP II STANDARDS.

Element	Compound	Factor ⁽¹⁾ (gms)	Factor x 10 ⁻² ⁽²⁾ (gm)
As	As ₂ O ₃	1.3203	0.0132
Au	Au ₂ O ₃	1.1218	0.0112
Ba	BaCl ₂	1.5163	0.0152
Co ⁽³⁾	Co ₃ O ₄	1.3620	0.0136
Ge	GeO ₂	1.4408	0.0144
Hf	HfO ₂	1.1793	0.0118
Hg	HgO	1.0798	0.0108
Ir	Ir	1.0000	0.0100
Nb	Nb ₂ O ₅	1.4305	0.0143
Os	Os	1.0000	0.0100
P	AlPO ₄	3.9372	0.0394
Pd	PdO	1.1504	0.0115
Pt	Pt	1.0000	0.0100
Re	Re	1.0000	0.0100
Rh	Rh	1.0000	0.0100
Ru	Ru	1.0000	0.0100
Sc	Sc ₂ O ₃	1.5338	0.0153
Sr	SrCl ₂	1.8092	0.0181
Ta	Ta ₂ O ₅	1.2211	0.0122
Te	TeO ₂	1.2508	0.0125
W	WO ₃	1.2611	0.0126
Y ⁽³⁾	Y ₂ O ₃	1.2699	0.0127
Total			0.2988

(1) Or weight of compound equal to one gram of element.

(2) Amount weighed equal to 0.01 gram of element.

(3) Cobalt and yttrium were included in both sets of standards to see if any difference could be detected in the presence of different impurities. None was detected.

Table 4
PREPARATION OF ALUMINUM STANDARDS FOR GROUP I.

Standard	Weight of Aluminum Metal or Aluminum Oxide (gm)	Weight of Added Impurities
1000X	0.9740 (metal)	0.0424 gm
100X	0.9000 (oxide)	0.1000 gm of 1000X
10X	0.9000 (oxide)	0.1000 gm of 100X
1X	0.9000 (oxide)	0.1000 gm of 10X

6. Continue as in Steps 5 - 8 of the procedure for converting aluminum metal to aluminum oxide.

7. Prepare a blank by dissolving about five grams of pure aluminum metal in the same way as described for the high standard.

Table 5
PREPARATION OF ALUMINUM STANDARDS FOR GROUP II

Standard	Weight of Aluminum Metal or Aluminum Oxide (gm)	Weight of Added Impurities
1000X	0.9780 (metal)	0.0299 gm
100X	0.9000 (oxide)	0.1000 gm of 1000X
10X	0.9000 (oxide)	0.1000 gm of 100X
1X	0.9000 (oxide)	0.1000 gm of 10X

8. Grind the appropriate amounts of standards and blanks, as listed in Tables 4 and 5, to form the complete sets of standards.
9. Excite the standards and develop the plates as described in the analytical procedure, Steps 1 through 4.
10. Examine the appropriate spectral lines (Tables 6 and 7) for proper gradation.

Table 6
DETECTION LIMITS FOR IMPURITIES IN ALUMINUM METAL
(Common Elements)

Element	Spectral Lines Used (Å)		Limit of Detection (µg Element/gm Sample)
Ag	3280.683		1
B	2496.778	2497.733	1
Be	3130.416		1
Bi	3067.716		10
Ca	4226.728		70(1)
Cd	3261.057		100
Co	3453.505		3
Cr	2835.633	2843.252	7
Cu	3247.540	3273.962	100(1)
Fe	2599.396	2483.270	10
Ga	4172.056		1
In	3256.090		10
Mg	2795.53	2802.695	10(1)
Mn	2593.729	2605.688	1
Mo	3132.594	3170.347	10
Ni	3414.765	3101.554	7
Pb	2833.069		10
Sb	2598.062		100
Si	2881.578	2516.123	100(1)
Sn	2863.327		10
Ti	3349.035	3361.213	1
V	2767.87	3519.24	70
V	3102.299		1
Y	3710.290	3242.280	1
Zn	3345.020		100
Zr	3391.975	3438.230	10

(1) Base material contamination; lower detection limit probable.

Table 7
DETECTION LIMITS FOR IMPURITIES IN ALUMINUM METAL
(Less Common Elements)

Element	Spectral Lines Used (Å)		Limit of Detection (µg Element/gm Sample)
Au	2675.95		10
Ba	4554.042		10
Ge	2651.178	2709.626	10
Hf	2820.224	2940.772	50
Nb	3163.402	3194.977	10
Pd	3404.580		1
Pt	3064.712	2659.454	10
Re	3460.46		10
Rh	3434.893		1
Sc	4246.829		1
Sr	4215.524		1
Ta	2714.674		100
W	4008.753		10

DISCUSSION

Preparation of suitable samples and standards was a major problem in this analysis. Anticipated samples for analysis would not be amenable to the traditional spark method; and, in addition, no metal standards are available for the many elements desired. To prepare such metal standards would be a project of considerable magnitude since uniform distribution of the impurities must be assured, losses prevented, and the impurity values verified by chemical analysis.

These circumstances necessitated a conversion of the sample into some other form, such as the oxide, into which adequate standards could be incorporated. Such a conversion should be achievable by dissolving the aluminum and thermally decomposing the resulting salt into aluminum oxide. As a choice for acid dissolution of aluminum, nitric acid is essentially without effect; hydrochloric acid dissolves most aluminum alloys, but becomes passive with very-high-purity material; strong sulfuric acid attacks high-purity aluminum at a significant rate; and, most effectively, aqua regia will dissolve both alloyed and high-purity aluminum. Aqua regia dissolution, therefore, appeared the most desirable approach provided contaminant losses were not encountered.

The aqua regia dissolution rate was adequate when sufficient surface area was present. A gram portion of shavings from a metal bar labeled 99.99+% aluminum was dissolved in a half hour. In contrast, a 1.3-gram, 1/4-inch-diameter bar of aluminum of about the same purity took about a week to dissolve.

The aqua regia solution was taken to dryness and then evaporated twice more with nitric acid to expel any chlorides before heating the residue to a high temperature.

Metallic chloride losses can be encountered at relatively low temperatures; metallic nitrates tend to decompose on heating.

Wet standards were prepared and ignited at 350, 800, and 1050° C to find a temperature high enough to expel the water and form a type of aluminum oxide that would not reabsorb enough moisture to lessen the sensitivity of the impurity detection.

The limits of the impurities detected in the 350° C material were not as low as in the materials heated to 800 and 1050° C. The latter were comparable with the detection limits of the dry-mix standards, so 850° C was selected as the ignition temperature for samples.

The materials heated to 350 and 800° C were amorphous (X-ray diffraction) while the material heated to 1050° C was a mixture of amorphous and crystalline material. A reported dependency on the crystallinity of the residue⁽²⁾ was not confirmed.

Standards were also dissolved in sulfuric acid and ignited at 1250° C, as recommended by MacCormac.⁽²⁾ The residue was crystalline aluminum oxide, but significant losses of silver, boron, cadmium, copper, lead, antimony, thallium, gold, iridium, osmium, rhenium, ruthenium, and tellurium were encountered. In addition, slight losses were noted for indium, molybdenum, vanadium, zinc, germanium, palladium, and rhodium. The parallel investigation of the sulfate approach was not pursued further since satisfactory performance was achieved with the aqua regia method. A more realistic ignition of the sulfate residue might have been obtained at the 850° C level, as reported by Degtjareva.⁽³⁾

A set of reference standards was prepared by dry mixing the impurities into aluminum oxide. These standards were used for comparison to ascertain any impurity losses resulting from the dissolution-ignition steps.

Wet standards were prepared following the sample-preparation procedure. The same impurity mixture used in the dry mix was added to aluminum metal and the mixture decomposed in aqua regia. Some of the impurities dissolved and some slurried, but adequate mixing was attained for all. Comparison of the resulting spectra indicated that osmium and mercury were completely lost and ruthenium and iridium were partially lost in the wet preparation. Consequently, these four elements were omitted from Table 7 as they are not correctly detected by this method. They were detected between 10 and 100 µg/gm Al in the dry preparation.

Since only these four elements behave differently when the standards are prepared by the dry instead of the wet method, there is little point in using the wet method for more than the initial set of standards.

All of the weights given in the tables of this report were for preparing standards by the wet method using aluminum metal. For the standards prepared by the dry mixing with aluminum oxide, the same values of the impurities were mixed with the appropriate amount of aluminum oxide ($\text{Al} \times 1.89 = \text{Al}_2\text{O}_3$).

Three elements included in Table 3 were not satisfactorily detected even in the standards prepared by dry mixing, namely: phosphorus ($> 1000 \mu\text{gs/gm Al}$), arsenic, and tellurium (around $700 \mu\text{gs/gm Al}$). These detection limits were not surprising since these elements are not generally sensitive to spectrographic detection.

Aluminum oxide, when burned alone in the DC arc, tends to form spheres which roll off the electrode. This action was prevented by mixing 35 milligrams of graphite with 20 milligrams of alumina. Lesser amounts of graphite were tried but even at a ratio of 1.5 graphite to 1 alumina, an occasional loss was noted. Unvented charges frequently spewed out of the electrode, but no losses of the electrode charges were encountered when properly vented.

Some other types of electrodes were investigated but none gave detection limits quite as good as the $3 \frac{1}{2} \times 8 \frac{1}{2}$ mm-crater electrodes recommended in this report. These electrodes, currently received under NCC Catalog Item SP 9019, appear identical to the NCC Catalog Items SP 9004 and 1570 referred to in previous reports from this laboratory.

No aluminum samples as such have been received. Ten samples of aluminized Mylar, converted in the Plant Laboratory to aluminum oxide, were analyzed by this method. All were found to be quite impure in the common elements. Chemical analyses for iron, copper, and titanium were available for some of these samples. The results for copper and titanium compared favorably, as seen in Table 8. The iron contamination exceeded the range for adequate spectrographic estimation.

Table 8
COMPARISON OF SPECTROGRAPHIC AND WET CHEMICAL RESULTS

Sample	Cu $\mu\text{gs/gm Al}$		Fe $\mu\text{gs/gm Al}^{(1)}$		Ti $\mu\text{gs/gm Al}$	
	Spectrographic	Wet Chemical	Spectrographic	Wet Chemical	Spectrographic	Wet Chemical
3001	100	97	2000	2667	-	-
3006	100	70	2000	2880	100	145
3007	100	48	2000	3400	100	145
3008	1000	1265	2000	4490	70	40
3009	100	71	2000	3220	200	254

(1) All iron values estimated since $1000 \mu\text{gs/gm Al}$ is the highest standard used.

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