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QUANTITATIVE DETERMINATION BY THE STALLWOOD AIR-JET DC ARC TECHNIQUE

4. TRACE IMPURITIES IN ALUMINUM, MAGNESIUM, TIN AND ZINC

by

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SUMMARY OF RESULTS

Trace impurities in aluminum, magnesium, tin and zinc metal can be adequately determined by a quantitative modification of the normal Stallwood Air-Jet dc Arc Technique.

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INTRODUCTION

The purpose of the investigation was to evaluate the applicability of the Stallwood Air-Jet dc Arc Technique (1, 2, 3, 4, 5, 6) for the determination of impurity elements in aluminum, magnesium, tin and zinc using as sample the metallic filings directly, without any chemical treatment.

OUTLINE OF THE METHOD

Spectra of the chosen standards of aluminum, magnesium, tin and zinc were obtained according to the normal Stallwood procedure. The intensities of the analytical lines were measured by the Sturrock Cathode Ray Densitometer. Working curves were prepared for the impurity elements by plotting the intensity ratios of the analytical line pairs against concentration on log-log graph paper. The percentage lower limits of determination for the impurity elements were evaluated from the curves and the densitometer readings.

APPARATUS AND MATERIALS

Excitation Source

Excitation was obtained from an A.R.L. dc Arc Source Unit Type No. 02825 A.

Spectrograph

Baird 3 metre grating spectrograph having a reciprocal dispersion of 5.5 A/mm.

Microphotometer

The intensities of the spectrum lines were measured by the Sturrock Cathode Ray Densitometer.

Photographic Processing Equipment

The plates were developed in a thermostatically controlled A.R.L. developing machine and dried on an A.R.L. plate dryer.

Sample Preparation Equipment

The samples were filed by a high speed motor-driven steel burr.

Standards

ALCOA high purity aluminum standards, DOW magnesium-base standards, NBS spectrographic tin standards and NBS spectro-

graphic zinc-base standards were used for preparing the working curves. The compositions of these standards are given in Tables 1, 2, 3 and 4.

TABLE 1

Per Cent of Impurity Elements in Aluminum Standards

ALCOA High Purity No.	Cu	Fe	Si	Mg
SA 663	0.045	0.066	0.074	
SA 664	0.082	0.094	0.068	
SA 799	0.0022	0.0026	0.0016	0.0009
SA 802	0.006	0.003	0.044	0.0009
SA 813	0.034	0.0056	0.0062	
SA 814	0.0052	0.0081	0.0088	
SA 815	0.016	0.012	0.015	

TABLE 2

Per Cent of Impurity Elements in Magnesium Standards

DOW No.	Cu	Fe	Si	Mn	Al	Zn	Pb
22387	0.011	0.033	0.006	0.004	0.007		
22388	0.0007	0.035	0.005	0.089	0.003		
22389	0.007	0.04	0.011	0.023	0.006		
13095	0.001	0.005	0.001	0.17	6.2	3.13	
51065		0.0008	0.02	0.12	5.39	0.29	0.025

TABLE 3

Per Cent of Impurity Elements in Tin Standards

NBS No.	Cu	Pb	As	Sb	Ni	Zn	Ag	Bi	Cd	Co
831	0.19	0.19	0.16	0.19	0.038	0.041	0.015	0.02	0.02	0.021
832	0.097	0.094	0.075	0.095	0.02	0.02	0.0095	0.0098	0.0095	0.0011
833	0.055	0.055	0.047	0.05	0.0095	0.0095	0.0055	0.0052	0.0053	0.0045
834	0.019	0.022	0.019	0.019	0.0044	0.0046	0.0018	0.002	0.002	0.002
835	0.0077	0.015	0.009	0.01	0.0024	0.002	0.001	0.0011	0.0011	0.0011
Misc No. 1		0.0017	0.0004	0.007				0.00005		
Misc No. 3	0.0001	0.001	N.D.	0.003				N.D.		

N.D. = none detected

TABLE 4

Per Cent of Impurity Elements in Zinc Standards

NBS No.	Cu	Al	Mg	Fe	Pb.	Cd	Sn	Cr	Mn	Ni	Si
625	0.035	3.06	0.07	0.035	0.0014	0.0006	0.0005	0.013	0.031	0.019	0.018
626	0.055	3.57	0.02	0.105	0.0021	0.0014	0.0011	0.039	0.048	0.048	0.042
627	0.135	3.89	0.03	0.023	0.0082	0.0049	0.0042	0.004	0.014	0.003	0.024
628	0.61	4.61	0.009	0.066	0.0044	0.0041	0.0017	0.009	0.009	0.03	0.009
629	1.50	5.16	0.094	0.016	0.013	0.015	0.012	0.0008	0.002	0.008	0.078
630	0.98	4.3	0.03	0.022	0.0083	0.0048	0.004	0.003	0.011	0.003	0.023

Electrodes

The upper electrode was a National Carbon Co. high purity graphite rod L 3803, 1/8 in. diameter with a pointed end, and the lower electrode a 1/8 in. diameter graphite rod with a 0.086 in. diameter hole drilled to a depth of 1 in.

Photographic Materials

Eastman Kodak Spectrum Analysis No. 2 plates were used for recording the spectra. Eastman Kodak D-19 developer and F-10 fixer were employed for developing the plates.

EXPERIMENTAL DETAILS

Electrode System

Ten milligrams of the prepared filings of the metal standard and 40 mg of National Carbon Co. SP-1 graphite powder (100 mesh) were weighed in a rhodium-plated dish, mixed well with a graphite rod and transferred to the graphite electrode cup by means of a rhodium-plated funnel. The electrode was sealed on the top with a small drop of celluloid solution and was then placed in the lower, positive electrode holder. The pointed electrode was placed in the upper, negative electrode holder.

Excitation, Exposure and Photographic Processing

The excitation of the electrodes, the recording of the spectra and the processing of the photographic plates were done under the conditions stated below.

(a) Conditions of Excitation and Exposure:

Source of excitation:	dc arc
Arc current:	6 amperes
Line voltage:	200 volts
Spectral region:	2200-3500 A
Slit width:	0.025 mm
Stepped sector:	1-10-100% rotary
Separation of electrodes:	2 mm (continually adjusted by means of back projection screen arrangement)
Electrode-holder:	water cooled
Pressure of the air jet:	3 in. of mercury
Arc preburn:	none
Arc exposure period:	complete burning indicated: (1) by the change in the colour of arc and shape of electrodes and (2) by the change in the noise of arc due to increase in the rate of burning.

(b) Conditions of Photographic Processing:

Emulsion:	Eastman Kodak S.A. No. 2 plates
Developing:	Eastman Kodak D-19; rocked for 6 min at 20°C
Stop bath:	water; rocked for 15 sec
Fixing:	Eastman Kodak F-10; rocked for 10 min
Washing:	running water for 30 min
Drying:	stream of hot air from the A.R.L. plate dryer

Photometry

The intensities of the analytical lines were measured on a Sturrock Cathode Ray Densitometer. The wavelengths of the analytical lines chosen for each impurity element in aluminum, magnesium, tin and zinc are given in Tables 5, 6, 7 and 8.

Working Curves

Working curves were prepared for each impurity element by plotting the concentration against the intensity ratio of the analytical line to the internal standard line on a log-log (3 x 2 cycles) graph paper.

Lower Limits of Determination of Trace Impurities

The lower concentration limits that can be satisfactorily determined by the standard Stallwood procedure were evaluated for all trace impurities detected in the chosen standards of aluminum, magnesium, tin and zinc and are reported in Tables 5, 6, 7 and 8.

TABLE 5

Lower Limits of Determination of Trace Impurities in Aluminum by Stallwood Method

Element	Wavelength in A	Percentage Lower Limit of Determination
Aluminum	3059.9	Principal Constituent - Internal Standard
Copper	3273.96	<0.002
Iron	3020.64	0.002
Silicon	2881.58	0.002

TABLE 6

Lower Limits of Determination of Trace Impurities present in Magnesium by Stallwood Method

Element	Wavelength in A	Percentage Lower Limit of Determination
Magnesium	3073.99	Principal Constituent - Internal Standard
Copper	3247.54	0.0007
Iron	3020.64	0.0008
Silicon	2881.58	0.001
Manganese	2593.73	0.004
Aluminum	3082.16	0.003

TABLE 7

Lower Limits of Determination of Trace Impurities present in Tin by Stallwood Method

Element	Wavelength in A	Percentage Lower Limit of Determination
Tin	3141.8	Principal Constituent - Internal Standard
Copper	3247.54	0.0005
Lead	2833.07	0.005
Arsenic	2349.84	0.02
Antimony	2598.06	0.005
Nickel	3414.8	0.005
Zinc	3349.29	$<$0.04 (not detected)
Silver	3382.9	0.002
Bismuth	3067.72	0.002
Cadmium	2288.02	0.005
Cobalt	3453.5	0.005

TABLE 8

Lower Limits of Determination of Trace Impurities present in Zinc by Stallwood Method

Element	Wavelength in A	Percentage Lower Limit of Determination
Zinc	2684.16	Principal Constituent - Internal Standard
Copper	3273.96	<0.03
Magnesium	2779.82	<0.009
Iron	3020.64	<0.01
Lead	2833.07	0.004
Cadmium	2288.02	0.004
Tin	3175.05	0.002
Chromium	2835.6	0.003
Manganese	2794.82	<0.002
Nickel	3414.8	0.008
Silicon	2881.58	<0.009

CONCLUSIONS

The results of this investigation show that the normal Stallwood dc Arc Technique can be employed satisfactorily for the determination of trace elements in aluminum, magnesium, tin and zinc. Since the procedure does not require any chemical treatment of the metallic filings, sample preparation is simple and the chances of contamination during the sample preparation are minimized.

REFERENCES

1. B.J. Stallwood, "Development of a General Method for the Spectrographic Analysis of Powder Samples" Thesis, University of Toronto (1951).

2. B.J. Stallwood, J. Opt. Soc. Am., 44, 171 (1954).

3. R.F. Sturrock and F.A. Lang, "Semiquantitative and Quantitative Spectrographic Analysis with the Stallwood Air-Jet Source", 1st Ottawa Symposium on Applied Spectroscopy, Mines Branch, Ottawa, September 20, 1954.

4. A.H. Gillieson, "Quantitative Determination by the Stallwood Air-Jet dc Arc Technique. 1. Trace Impurities in Titanium Oxide", Mines Branch Investigation Report IR 61-48, Department of Mines and Technical Surveys, Ottawa (1961).

5. K. Bhaskara Rao and A.H. Gillieson, "Quantitative Determination by the Stallwood Air-Jet dc Arc Technique. 2. Trace Impurities in High Purity Copper", Mines Branch Investigation Report IR 61-80, Department of Mines and Technical Surveys, Ottawa (1961).

6. Elisabeth M. Kranck, "Quantitative Determination by the Stallwood Air-Jet dc Arc Technique. 3. Trace Impurities in High Purity Gold", Mines Branch Investigation Report IR 61-81, Department of Mines and Technical Surveys, Ottawa (1961).

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