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QUANTITATIVE DIRECT-CURRENT ARC ANALYSIS OF RANDOM COMPOSITIONS OF MICROGRAM RESIDUES IN SILVER CHLORIDE COMMON MATRIX

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16. Abstract

A procedure is described for spectrochemical analysis of random compositions of 20 elements in the concentration range from 0.1 to 100 percent. Samples are microgram residues derived from dissolution of metal samples. Calibration curves, one for each element, are prepared over the range from 0.01 to 10 micrograms. Absolute amounts of analyte elements and their percentage concentration are determined from these curves for all compositions. Analyses of some alloy standards with and without use of comparison standards are reported as examples of results attainable. No matrix effects attributable to excitation suppressions or enhancements were found.

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SUMMARY

A spectrochemical procedure is described for quantitatively determining random combinations of 20 programmed elements. The programmed elements are Al, Co, Cr, Fe, Hf, Mn, Mo, Nb, Ni, Pd, Re, Si, Ta, Ti, Th, U, V, W, Y, and Zr. The response of a direct-reading spectrometer is calibrated for absolute amounts of each of these elements alone over the range from 0.01 to 10 micrograms. Absolute amounts of elements in the sample are determined from these calibration curves, with correction made for background and spectral line interferences. Percentage compositions are calculated from the absolute amounts of analyte elements determined.

The analytical samples are dissolved and microliter amounts of the solutions are deposited onto carbon electrodes. The carbon electrodes are specially prepared to contain 4 milligrams of silver chloride (AgCl) in the carbon matrix. The silver chloride serves as a buffer material and also as a common matrix. The electrodes are arced in agron, which results in the vaporization and excitation of the metal constituents in the residue. With a minimum AgCl-to-sample weight ratio of 400, no matrix effects attributable to excitation suppressions or enhancements were found.

Analyses of some alloy standards with and without use of a comparison standard are reported as examples of results attainable by the procedure. With automation of sample arcings and data reduction, the analysis time is about 4 minutes per sample, including preparation of electrodes through data recording but not including sample dissolution.

INTRODUCTION

The need for appropriate comparison standards in emission spectrochemical analysis is the single most limiting characteristic of the method. The root cause of the problem is the complex effects of sample composition on atomic emission. In this report, as is customary in the field, the term matrix effect is used to denote any mechanism which either increases or decreases the atomic emission from a given amount of analyte element in the sample. The origins of matrix effects are discussed in references 1 and 2. Because of these effects, the samples must accurately simulate the chemical and physical forms of the comparison standards. Much effort is required to prepare standards and validate procedures, often for relatively minor changes in sample composition. As a result, the emission method is inefficient and uneconomical in many analytical applications, particularly those of a nonroutine nature.

The ideal solution to this problem is to calculate chemical compositions theoretically from measurements of emitted light intensities. Some progress has been made in this approach in recent years (ref. 3). However, because of the complexities and instabilities of the vaporization and excitation phenomena in the arc discharge, this approach has not resulted in a practical method for spectrochemical analysis.

Another approach to the problem is to reduce the unknown samples to a common chemical and physical form. Calibration standards of the same form as the samples can then be used for all sample compositions. Many practical spectrochemical methods have been described which use this principle. The most effective procedure is to dilute the sample in a relatively larger mass of a pure material, and then excite the spectra with a direct-current arc. The dilution can be achieved by either mechanical blending of powders (ref. 4), or by fusing the sample with the diluent (ref. 5). With proper selection of the diluent, a common environment is provided for all sample compositions.

The effectiveness of this approach is dependent on a high diluent-to-sample ratio. Ratios higher than 100 parts diluent to 1 part sample are desirable but, because of the insufficient detectability of the arc, the dilution ratio is limited to the order of 10 parts diluent to 1 part sample. Because of the low dilution ratios, these methods are best applied to sample types having relatively small variations in composition, rather than to random compositions of elements. Furthermore, due to errors associated with arc excitation, the methods have been semiquantitative, with errors ranging from about 30 percent to 100 percent of the amount present.

The method described in this report is applicable for quantitative analysis of random compositions of 20 programmed elements. Analytical results are derived from single-element calibrations for each of the programmed elements. Calibration curves of absolute amounts of each element, ranging from 0.01 to 100.0 micrograms, are permanently filed. Percentage compositions are calculated from the absolute amounts determined. No internal standards are used and a single analytical line for each element is used for at least three decades of concentration. Corrections for spectral line interferences can be made with no foreknowledge of them. The method is applicable to samples as small as 10 micrograms and the sample weight need not be known. If the sample weight is known, a mass balance with respect to metal constituents can be calculated.

The advantages of this procedure derive from refinements of the arc source (refs. 6

to 8). In reference 6, conditions are reported for detecting nanogram amounts of elements in the argon arc in the presence of milligram quantities of silver chloride (AgCl). Because of the good detectability of analyte elements in the presence of larger quantities of AgCl, dilution ratios of 1 to 400 are feasible with AgCl serving as a common matrix. The use of a tantalum (Ta)-tipped cathode for eliminating errors caused by arc wander is described in reference 7. In reference 8, a method is described for controlling either arc light intensities or arc current. In the present work, the arc current was controlled according to a time-dependent program. Recently, the authors developed a carbon anode which provides quantitative vaporization of microgram samples into the argon arc. The results of this work are discussed in the appendix. All of these developments were combined in the analytical procedure described herein.

The most important characteristic sought in the development of this procedure was freedom from matrix effects, particularly those associated with excitation in the arc column. A secondary, but still important, consideration was the economy and speed of the determinations. The procedural steps of the method were established so that they are simple, rapid, and amenable to automation, insofar as possible. After sample dissolution, about 4 minutes per sample are required through recording of data. The excitation sequence of 11 samples in the arc chamber is completely automated, as is the reduction of data. However, detailed description of the automation is not within the scope of this report. Reference to certain features of the automation is made only to facilitate understanding of the total analytical concept.

INSTRUMENTS AND PROCEDURES

The instruments used in this work consisted of a specially developed arc chamber, a conventional direct-reading spectrometer, and a Lewis developed paper tape data recording system. The primary characteristics of the spectrometer are summarized in table I, along with pertinent operational information. The arc chamber, illustrated in figure 1, was described in detail in references 7 and 8. A description of the data recording system and computer programs is in preparation.

The operation cycles of the arc chamber, spectrometer, and recording system are programmed so that 11 samples are arced in sequence and the data recorded without attendance by an operator. The sample electrodes are specially prepared to contain 4 milligrams of AgCl intimately mixed with a residue containing 10 micrograms of sample. These electrodes are loaded into the arc chamber and arced according to the sequence shown in figure 2. The time-variable current program is shown in figure 3. After an initial arcing time of about 5 seconds at a current of 11 amperes, the current is gradually increased to the maximum current of about 36 amperes. Also shown in figure 3 is the

TABLE I. - SUMMARY OF EXPERIMENTAL CONDITIONS

Spectrometer:	
Dispersion, Å/mm	5.6
Focal length, m	1.5
Entrance slit width, μm	25
Exit slit width, μm	75
Photomultiplier tubes	Spectral response, S-4 and S-5; applied voltage, 750 to 950 V
Excitation atmosphere:	
Fill gas	Argon (99.99 percent), static atmosphere renewed for each sample
Pressure (initial), torr	300
Electrodes:	
Anode	High-purity carbon (fig. 4)
Cathode	Ta-tipped graphite rod (ref. 7)
Anode-cathode spacing, mm	13
Sample	Ten-microgram residue, from aliquot of dissolved sample, added to anode with 4 milligrams AgCl precipitated in carbon matrix
Arc current (time dependent), A	11 to 36 (fig. 3)
Arcing sequence	As shown in figure 2
Calibration	Pure solutions of single elements containing 0.01, 0.03, 0.1, 0.2, 0.5, 1, 2, 5, 10, and 100 micrograms of metal per 10 microliters

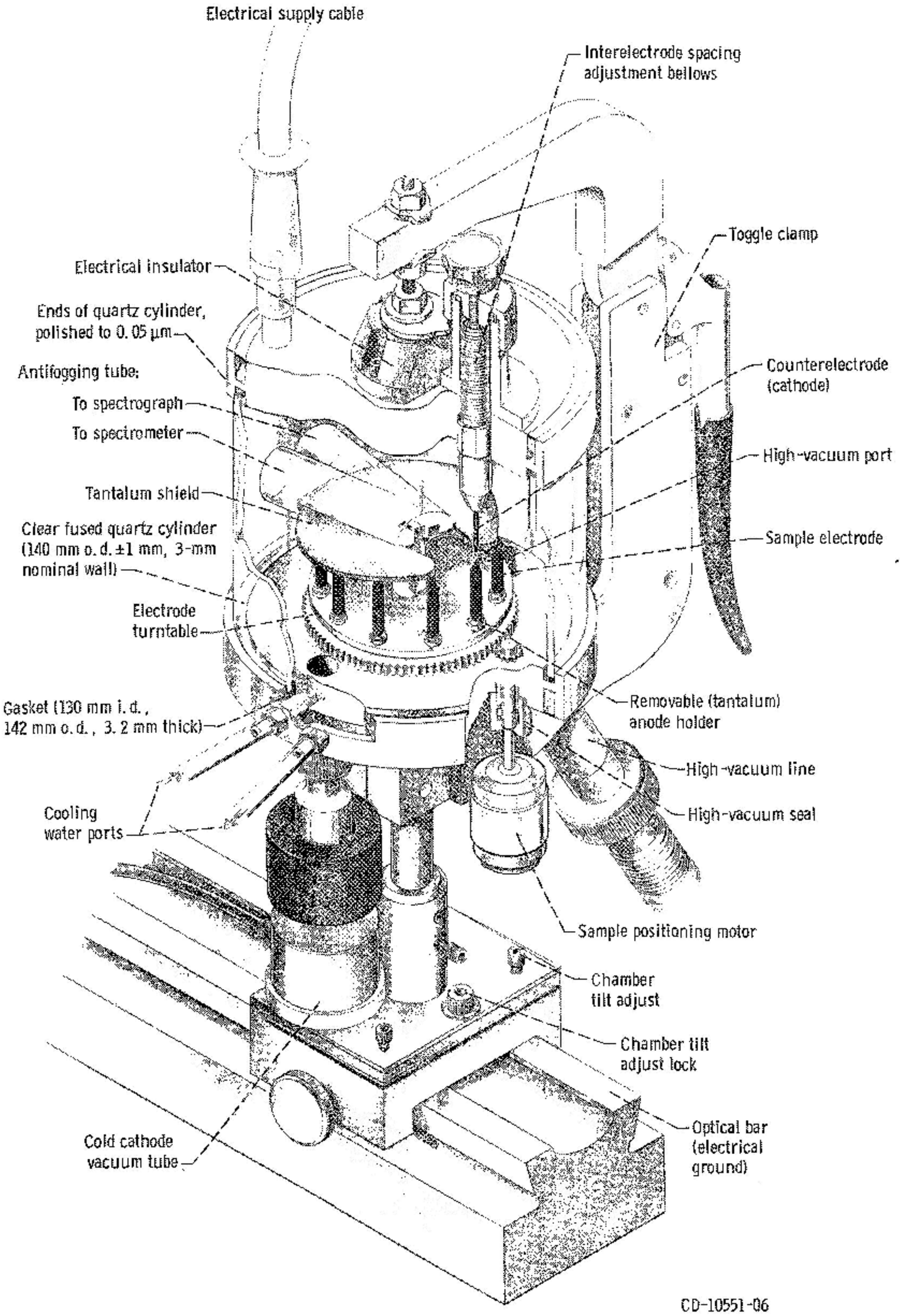

Figure 1. - Controlled-atmosphere arc chamber. (Top of chamber is at high voltage during instant arc is spark ignited. Precautions must, therefore, be taken to prevent contacting chamber top at this time.)

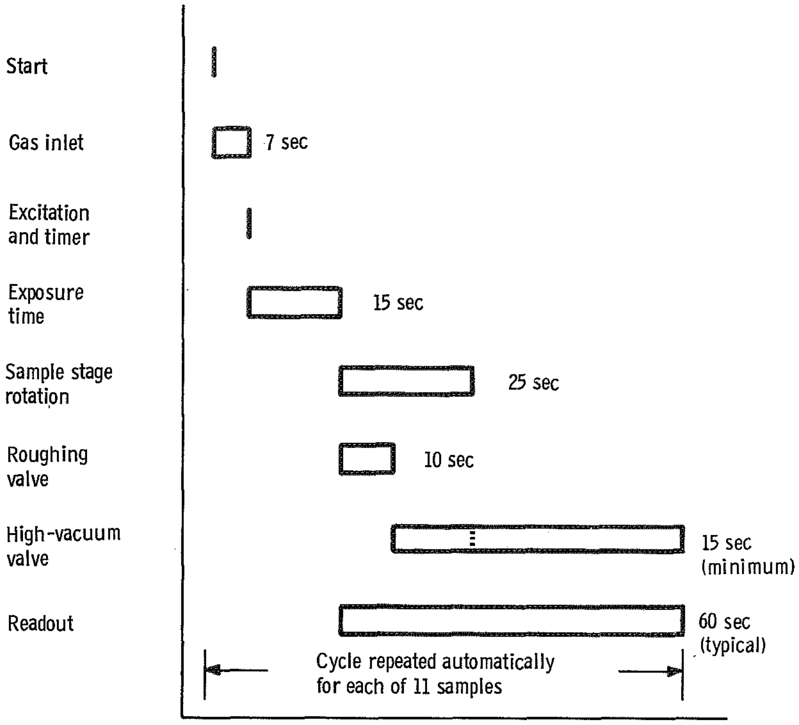

Figure 2. - Generalized operating sequence for controlled-atmosphere arc.

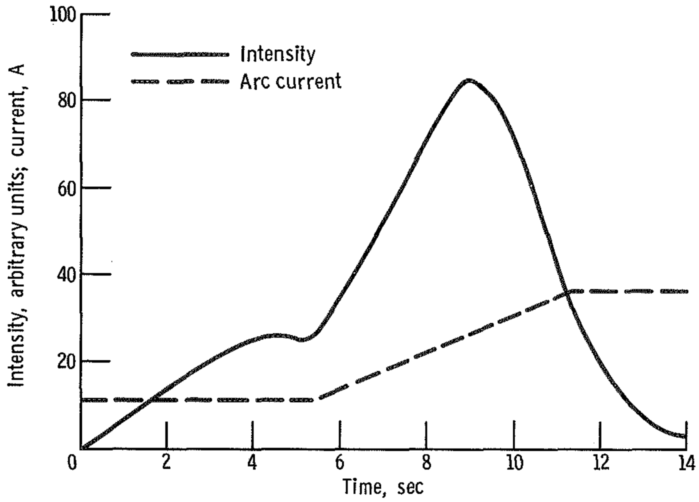

Figure 3. - Intensity-time profile for 4 milligrams of silver chloride, and arc current program.

typified time-intensity profile for 4 milligrams of AgCl. All of the analyte elements are vaporized within this profile.

Electrodes

Cathode. - The cathode is the Ta-tipped graphite rod described in reference 7. The use of this cathode eliminates the arc wander normally observed with the free-running arc. Each cathode was used for 100 to 200 arcings with no intervening treatment, except to wipe the deposits from the graphite supporting rod after each arcing sequence (11 samples).

Anode. - The anodes are carbon (not graphite) rods 4.57 millimeters in diameter and about 38 millimeters in length. The tip was formed to a 90° point. The carbon anodes were preformed from the highest-purity material that was commercially available. The special characteristics of this anode configuration are discussed in the appendix.

Procedures for Preparation of Samples and Electrodes

Addition of 4 milligrams of AgCl to carbon anodes. - High-purity carbon electrodes, either as obtained from a commercial supplier or purified as described in the following

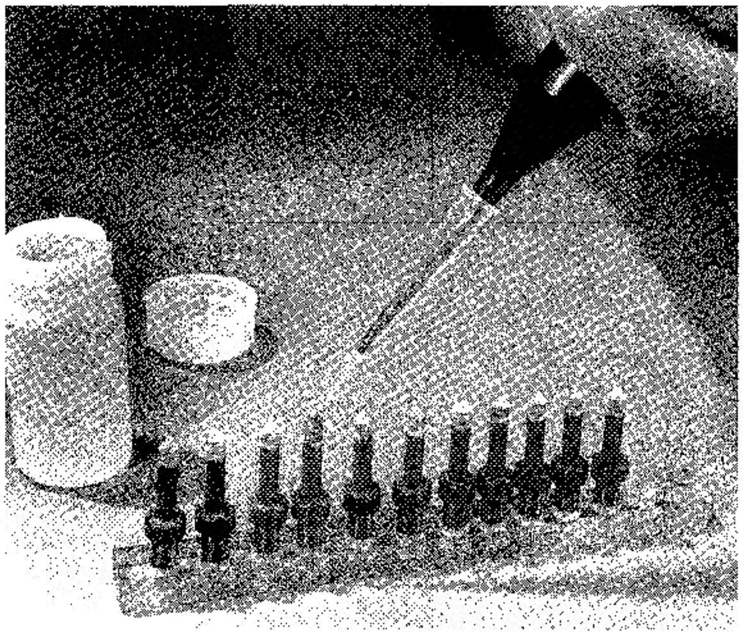

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Figure 4. - Doping of 10 microliters of sample aliquot onto carbon anodes containing 4 milligrams of silver chloride.

section, are treated to contain 4 milligrams of AgCl. This is done by a two-step doping of silver nitrate ($AgNO_3$) and hydrochloric acid (HCl) solutions on the electrodes to precipitate AgCl in the carbon matrix. A 10-microliter plastic pipette (shown in fig. 4) having a dispensing accuracy of better than 1 percent is used for dispensing the liquids.

In the first step, 10 microliters of a 2.8-normal $AgNO_3$ solution are added with the pipette to the annulus of the electrodes near the point. The liquid penetrates into the electrode and is allowed to equilibrate for 2 minutes. After this time, 10 microliters of 6-normal HCl are added in the same way as the $AgNO_3$. The precipitation reaction is allowed to equilibrate for about 7 minutes at room temperature before the electrodes are dried at 90° C for 3 minutes. The AgCl is normally localized in the upper 5 millimeters of the electrodes. The appearance of the AgCl residue can be seen in figure 4.

After addition of AgCl, the electrodes are ready for the addition of sample solutions.

Addition of samples to carbon anodes. - Samples in the form of alloys or miscellaneous samples, including surfaces of solid specimens, are dissolved in acids. The amount of sample taken is the minimum that is representative of the analytical specimen. When the minimum representative sample is not known, the amount dissolved is at least 0.25 gram. Five acids or acid mixtures were used for dissolution of all metal alloys analyzed:

(1) Three parts 48-percent hydrofluoric acid (HF) and 1 part 70-percent nitric acid (HNO_3)
(2) Three parts 38-percent HCl and 1 part 70-percent HNO_3
(3) Thirty-eight-percent HCl
(4) Seventy-percent HNO_3
(5) Forty-eight-percent HF

The appropriate acid mixture and dissolution conditions must be determined for the composition of interest.

Special precautions must be taken when determining silicon (Si) or rhenium (Re). If Si is to be determined, acid mixtures containing HF are used and Si may be lost as silicon tetrafluoride (SiF_4). In this case, the dissolution is done in a capped plastic bottle on a steamtable. Excess pressure is periodically released by cooling to room temperature and uncapping the bottle. With care, escape of volatile compounds of Si can be avoided and Si can be determined. To avoid loss of SiF_4 when drying the sample residue at 90° C, ammonia vapor must be in contact with the liquid aliquot. This is accomplished by placing a small beaker of ammonium hydroxide under the plastic cover which contains the electrodes on the hotplate. If Re is to be determined, samples are dissolved on the steamtable, rather that at higher temperatures on the hotplate, to avoid loss of volatile Re compounds.

After dissolution, the sample solution is diluted to contain a definite metal concentration. Solutions diluted to contain 1 gram of metal per liter are used to determine metal concentrations between 0.1 and 100 percent in the sample. This concentration range corresponds to absolute amounts of metal between 0.01 and 10 micrograms, which is the maximum useful range of the calibration curves. Higher metal concentrations, to about 100 grams per liter, can be used for the concentration range from 10 ppm to 1 percent. However, when sample weights greater than 10 micrograms are used, a comparison standard must be used to compensate for matrix effects.

The 10-microliter aliquot of each sample is deposited on the pointed carbon electrodes that were previously prepared to contain 4 milligrams of AgCl as described in the previous section. Normally, the liquid immediately wets the electrode surface and penetrates into approximately the same volume as penetrated by the AgCl. After the samples are doped, the electrodes are dried for 3 minutes at 90° C. The sample doping operation is illustrated in figure 4. A discussion of the chemical nature of the residues is included in the appendix.

A series of electrodes prepared in this way is then loaded into the arc chamber and arced according to the sequence shown in figure 2. Replicates of 10-microliter aliquots from the dissolved samples can be arced to improve precision and accuracy.

Calibrations

Quantitative calibrations are made of spectrometer counts versus micrograms for each analyte element. The list of programmed elements, the wavelengths of the spectral lines, and excitation potentials of the lines are shown in table II. Standard solutions of each of the analyte elements are prepared by dissolving about 0.25 gram of each of the pure metals in either HCl or HF, with additions of HNO_3 as necessary to effect the dissolutions. The solutions are diluted to contain 10 grams of metal per liter (100 μg/10 μl). The next standard (10 μg/10 μl) is prepared from the first solution by a tenfold dilution with distilled water. The remaining series of standards are prepared by diluting an aliquot of one of the more concentrated standards. The minimum aliquots taken were 10 microliters and the minimum standard volume that was stored was 5 milliliters. The diluent used to successively dilute standards below 10 micrograms per 10 microliters was of the same acid composition as that of the 10-microgram-per-10-microliter standard. Therefore, the acid strengths of the standard solutions were the same, except for the highest standard (100 μg/10 μl), which had an acid strength 10 times that of the lower standards.

The standard solutions are stored in tightly capped plastic containers having a volume no more than twice that of the total volume of the standard solution.

Single-element calibrations were prepared from these standard solutions. Ten microliters of each of the standard solutions are added to the tip of the carbon anodes. Because the arc chamber contains 11 anode positions, the electrodes are processed in batches of 10 with a blank sample included with each series of samples. Calibration

TABLE II. - SUMMARY OF PROGRAMMED

ATOMIC LINES

Element and ionization state[a]	Wavelength, Å	Excitation potential, eV	
		Upper	Lower
AlI	3944.03	3.13	0
CoI	3453.51	4.00	.43
CrI	4254.35	2.90	0
FeI	3719.94	3.32	0
HfII	4093.16	3.47	.45
MnII	2576.10	4.79	0
MoI	3864.11	3.19	0
NbII	3094.17	4.50	.51
NiI	3566.37	3.88	.42
PdI	3634.7	4.21	.81
ReI	4889.15	2.52	0
SiI	2881.59	5.06	.78
TaI	2965.54	4.41	.25
TiII	3349.40	3.73	.05
ThII	4391.11	3.36	.55
UII	3859.58	3.24	.03
VII	3102.29	4.34	.37
WI	4008.77	3.44	.36
YII	3600.74	3.61	.18
ZrII	3391.96	3.80	.16

[a] I denotes neutral atom; II denotes first ionization state.

curves were obtained by four replicate arcings of the 10 standards for each of the 20 programmed elements. To minimize the possibility of contamination of lower standards by higher standards, the standards in each chamber load were grouped to cover a minimum microgram range. The standard groups were arced in order from the lower microgram amounts to the higher microgram amounts.

The standard samples are arced according to the sequence shown in figure 2 with the blank sample being arced first. All of the element channels of the direct-reading spectrometer are recorded for each standard. The response of the element channel being calibrated results in the analytical calibration curve for that element. The responses from the element channels other than the one being calibrated provide the necessary information for making automatic corrections for direct spectral line interferences.

The complete calibration data are used to construct a 20-by-20 matrix array of response curves: 20 element calibration curves and 380 interference response curves. Both the element calibration data and the interference data are curve fit by a computer procedure.

RESULTS AND DISCUSSION

Calibrations

The characteristics of the quantitative calibration curves for the 20 programmed elements are summarized in table III. All of the spectral lines listed were used over at least three decades of concentration corresponding to 0.01 to 10 micrograms. However, the calibrations also include a standard at 100 micrograms to improve the computer curve fit at the high end. The calibrations were obtained from four replicates of each of the 10 standard solutions and for each of the 20 elements. A rejection criterion was applied to this data which rejected individual results that were outside the 95-percent confidence limit.

Using the information in table III, approximate calibration curves can be constructed for each analyte element. (The calibration curve for titanium is shown as an example in fig. 5.) All of the background-corrected curves are approximately linear except in the higher microgram range. All of the curves exhibit slowly decreasing slopes down to zero slope at the maximum count level shown in column 8. Points for the lowest standard, maximum slope, the point of 30-percent nonlinearity, and maximum counts are shown in columns 3 to 8.

The error curves for these calibrations are typically U-shaped with the higher errors occurring at the 0.01- and 100-microgram standards. However, the 100-microgram standard is not recommended for use in analysis. Column 9 of table III shows the average relative standard deviation over the most precise microgram decade, and column 10 indicates the applicable decade. The highest relative errors were obtained for the lowest standard (0.01 μg) in every case. These precisions are shown in column 11. All of the precision data in table III were obtained over a period of several days.

The precisions over the optimum microgram range average about 7 percent for the 20 elements and occur generally in a middle portion of the calibration curves. In this region the instrument error is typically less than at either end of the calibrations.

The larger relative errors at the ends of the curves are caused by both source and instrument limitations. The instrument limitations occur because the dynamic range of the spectral lines exceeds that of the readout system. At the lower end of the curves the errors are caused by arc source noise and inadequate intensity resolution. The instrument error in this region typically ranges from about 3 to 10 counts for the various readout channels. In comparison with the counts obtained for the 0.01-microgram standard,

TABLE III. - SUMMARY OF RESULTS OF CALIBRATIONS

Element	Atomic line, Å	Response background-corrected counts at 0.01 microgram	Maximum slope	Micrograms at maximum slope	Micrograms at 130 percent of predicted concentration using maximum slope	Response at 130 percent of predicted concentration	Maximum response (background counts corrected)	Relative standard deviation[a]		
								Average over most precise decade range	Most precise microgram decade	At 0.01 microgram
Al	3944	26.6	1.125	0.500	0.888	2369	18 787	11	0.5 to 5.0	15
Co	3453	22.2	1.003	.500	.923	1562	12 666	6.7	0.5 to 5.0	39
Cr	4254	74.9	1.104	.100	.520	3098	15 237	5.1	0.1 to 1.0	116
Fe	3720	30.7	1.014	.500	.897	2378	16 187	6.2	1.0 to 10.0	59
Hf	4093	10.9	1.088	.100	.764	646	14 966	3.7	0.5 to 5.0	141
Mn	2576	39.3	1.019	.100	.755	2323	10 668	7.2	0.1 to 1.0	21
Mo	3864	26.9	1.285	.100	.428	1884	13 030	4.7	0.1 to 1.0	38
Nb	3094	19.3	1.096	.100	.564	1232	18 252	3.8	0.1 to 1.0	10
Ni	3566	16.6	1.113	.500	.911	1896	19 356	3.8	0.5 to 5.0	32
Si	2881	32.5	.982	.100	.779	2395	17 057	6.6	0.5 to 5.0	68
Ta	2965	25.1	1.167	.100	.793	2670	19 553	8.8	0.5 to 5.0	110
Ti	3349	107.9	.975	.100	.782	3671	17 964	6.5	1.0 to 10.0	58
Y	3600	10.0	1.027	.500	.898	1058	11 111	9.0	0.1 to 1.0	16
V	3102	35.5	1.024	.500	.893	2878	17 968	5.5	1.0 to 10.0	11
Th	4391	16.9	.969	.500	.949	1410	18 394	5.0	0.5 to 5.0	13
U	3860	0	.888	.500	.974	483	13 055	5.1	1.0 to 10.0	ND
W	4009	65.2	1.046	.100	.723	4163	20 030	2.3	1.0 to 10.0	64
Pd	3635	33.1	.959	.500	.880	2554	15 667	8.7	0.5 to 5.0	10
Re	4889	72.8	.870	.500	.917	2318	17 227	19.2	0.5 to 5.0	36
Zr	3392	69.4	.956	.500	.912	2454	17 814	5.9	0.1 to 1.0	48

[a] Relative standard deviation = $\dfrac{\sqrt{\dfrac{\sum (\text{deviations})^2}{\text{Number of samples} - 1}}}{\text{Sample mean}} \times 100.$

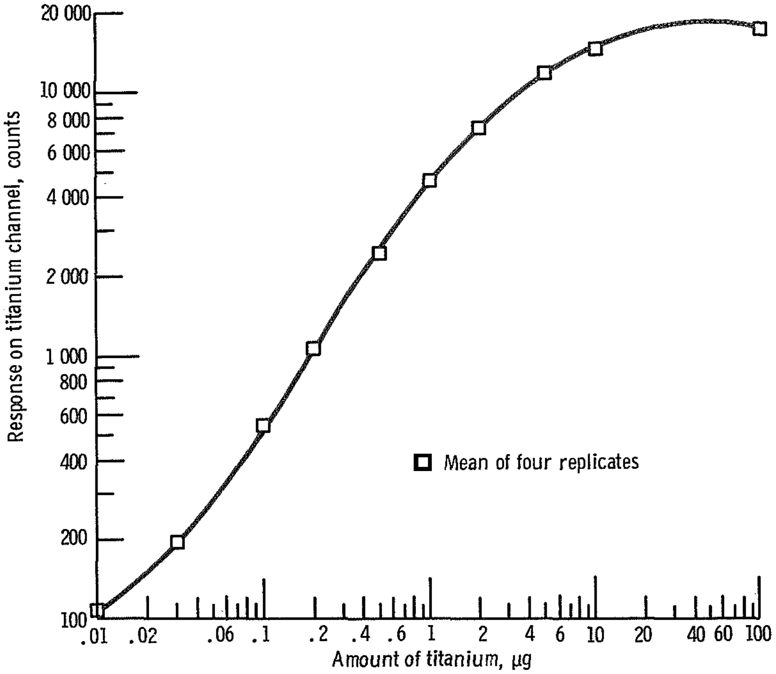

Figure 5. - Example calibration curve.

shown in column 3 of table III, this can account for significant errors in the low microgram region. In the higher microgram range, instrument nonlinearities, and to a lesser extent self-absorption, caused the higher relative errors at the 100-microgram level. In this higher region, the nonlinearities of the readout system gradually contribute to the relative errors and finally negate the usefulness of the spectral lines in the range between 10 and 100 micrograms.

For some common elements, a significant source of error is contamination. This is the primary limiting error for the elements Fe and Cr, which are also major constituents in the steel arc chamber. The contamination presumably occurs as a result of the corrosive reaction between the AgCl vapor and the arc chamber. The precisions of Si and Ta are also limited by transfer of materials in the arc chamber. Contamination of these elements is directly related to the amount of fluorine in the sample residue. These fluorides are almost always present in the samples because HF is used in the dissolution of samples. However, this source of error is not necessarily limiting when calibrating these elements because the amount of fluorides, relative to the analyte elements, is small and is also relatively constant for all standards. In the analysis of samples which have been dissolved in HF, the fluoride in the sample residue limits the precisions of determination of Si and Ta, especially at concentrations below a few percent in the sample.

To achieve the best precisions, the amount of sample placed on the anode can be adjusted so that a specific analyte element falls in the optimum microgram range indicated in column 10 of table III. Although this is advantageous for some analyses, it is done at the expense of range of analysis for other elements. Improvement of precision by replicate arcings of sample aliquots is also a practical approach because of the speed with which samples can be processed.

Analysis of Alloy Standards

The analyses of three alloy standards are summarized in table IV. The tabulated results are derived from averages of four replications with about 9 months of elapsed time between element calibrations and sample analyses. These alloys were selected for testing because they were the most compositionally complex standards available. The combination of elements in these standards represents a fairly random test with respect to properties of the elements and excitation characteristics of the spectral lines. Therefore, the analytical results obtained on these alloys are presumed to be typical of other combinations of analyte elements.

The standard percentages are those certified by the National Bureau of Standards. These percentages are compared with the determined percentages listed in the remaining columns. The results in these latter columns were obtained by the three methods of calculation described in the next section. These results are reported for three weights of sample residue, 10, 30, and 100 micrograms. Since the weight of AgCl was always 4 milligrams, the variation in sample weight provides a measure of the effect of the dilution ratio on analytical results. Thus, the sample-diluent ratios for 10, 30, and 100 micrograms are 1/400, 1/133, and 1/40, respectively.

The accuracies of the analyses in table IV are estimated by comparing the determined percentages with the standard percentages. In some cases the accuracies show significant variations exceeding the 95-percent confidence limit calculated from the precision data. Possible causes of these inaccuracies are discussed in the following sections.

<u>Calculation of percentage compositions</u>. - Percentage compositions were calculated from the microgram amounts of each element determined from the single-element calibration curves. Three methods are used in making these calculations, as shown in the following equations:

(a) Percentage determined relative to weight of sample added to electrode:

$$\text{Percentage} = \frac{M(d)}{M(a)} \times 100$$

(b) Percentage determined relative to weight of sample recovered:

TABLE IV. - SUMMARY OF TYPICAL ANALYTICAL RESULTS ON ALLOY STANDARDS

Sample	Element	National Bureau of Standards certified percentages	Weight of sample residue added to electrode, μg								
			10			30			100		
			(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
S-816 alloy (NBS 168)	Co	41.2	42.7	42.2	41.9	36.6	44.1	43.1	13.1	31.2	43.2
	Cr	20.33	22.6	22.3	21.7	15.4	18.5	23.4	3.97	9.51	22.0
	Fe	3.43	3.45	3.40	3.45	2.90	3.49	3.07	2.54	6.08	3.47
	Mn	1.50	1.60	1.58	1.32	1.46	1.77	1.29	1.10	2.62	1.40
	Mo	3.95	^{d}2.92	2.89	3.76	2.55	3.07	3.35	1.46	3.50	3.79
	Nb	2.95	^{d}2.46	2.44	2.79	2.16	2.61	2.81	2.01	4.80	3.05
	Ni	20.25	^{d}18.0	17.8	19.2	16.2	19.5	19.4	13.3	31.7	20.0
	Ta	.95	^{d}2.82	2.79	1.21	2.06	2.51	.94	1.06	2.53	1.07
	Ti	.06	Element not determined below 0.1 percent								
	V	.03									
	W	3.95	3.75	3.72	3.95	3.01	3.64	3.62	2.72	6.48	3.74
Co-Mo-W steel (NBS 153)	Co	8.45	^{d}7.12	7.26	8.05	9.45	12.0	8.89	6.41	18.7	9.02
	Cr	4.14	4.13	4.21	3.91	4.82	6.14	4.41	2.32	6.78	3.94
	Fe	^{e}73.9	74.3	75.7	75.6	52.9	67.4	75.2	15.9	46.4	76.1
	Mn	0.219	^{d}.11	.11	Not detected in standard	0.22	.29	.43	.18	.51	.41
	Mo	8.38	^{d}7.00	7.14	8.03	6.14	7.81	7.42	3.17	9.22	9.70
	Ni	.107	.10	.10	.10	.26	.33	.11	.21	.60	.10
	V	2.04	1.81	1.85	1.76	2.14	2.74	2.11	1.47	4.31	2.12
	W	1.58	^{d}1.45	1.48	1.32	1.51	1.93	1.67	1.09	3.18	1.54
Ferro-vanadium alloy (NBS 61A)	Al	0.02	Element not determined below 0.1 percent								
	Cr	.68	0.45	0.52	0.55	0.41	0.49	0.61	0.44	1.17	0.73
	Fe	^{e}41.0	^{d}39.8	45.9	42.4	31.9	37.9	41.1	13.1	34.4	39.2
	Mn	1.78	^{d}1.60	1.85	1.56	2.06	2.45	1.61	2.29	6.00	1.55
	Si	5.12	(f)	(f)	3.86	(f)	(f)	4.96	(f)	(f)	7.05
	V	50.2	^{d}53.5	61.7	49.6	42.5	50.6	48.8	12.7	33.6	50.1

[a] Percentage determined relative to weight of sample added to electrode.

[b] Percentage determined relative to weight of sample recovered.

[c] Percentage determined relative to comparison standard.

[d] Significant variation, exceeding 95-percent confidence limit, between this result and that of column (c).

[e] By difference.

[f] Absolute amounts of Si not determined due to volability of SiF_4.

$$\text{Percentage} = \frac{M(d)}{\Sigma M(d)} \times 100$$

(c) Percentage determined relative to comparison standard:

$$\text{Percentage} = \frac{M(d)}{f\Sigma M(d)} \times 100$$

where

$M(d)$	mass of analyte element determined
$M(a)$	mass of sample added to electrode
$\Sigma M(d)$	sum of masses determined for all analyte elements
f	matrix correction factor

These equations correspond to footnotes a, b, and c, respectively, of table IV. The correction factor f is derived from results on a synthesized comparison standard according to the following relation:

$$f = \frac{M(ds) \times \Sigma M(ps)}{M(ps) \times \Sigma M(ds)}$$

where

$M(ds)$	mass of analyte element determined in standard
$M(ps)$	mass of analyte element present in standard

Method (a) is based on absolute quantities of analyte elements and is accurate if the mass balance is 100 percent and if matrix effects are negligible. Method (b) assumes that the mass of nonprogrammed elements in the sample is negligible. This method can provide compensation for matrix effects caused by nonquantitative recovery of samples from the electrode. This method can be used to calculate percentages when the sample weight is not known, such as in the chemical analysis of surfaces. For 100-percent mass balance, methods (a) and (b) yield the same results. Method (c) provides compensation for matrix effects of all types but is less efficient than methods (a) and (b) because it requires preparation and arcing of a synthetic standard. Method (c) also provides compensation for system drift if the standards are arced with the samples. This method, therefore, serves as a basis for comparison in evaluating errors in the system, including matrix effects.

Estimation of matrix effects. - Matrix effects can be estimated by comparing the results given in table IV. Some results in column (a) of the 10-microgram sample weight are significantly different, exceeding the 95-percent confidence interval, from the results in column (c). Since the results in column (c) were obtained with the use of a comparison standard, they are not subject to matrix effects. Therefore, these differences are presumed to be caused either by systematic errors in the procedure for preparing standards and samples, or by matrix effects in the results of column (a). Differences between the standard (NBS) percentages and the results of column (a) can also indicate matrix effects. However, such comparison may be ambiguous because of long-term drifts occurring in the 9-month period between the calibrations and the analysis of samples of table IV.

By examining the trends in the comparative data of table IV, it is possible to estimate certain types of matrix effects related to excitation phenomena in the arc column. The matrix effect caused by variations in the excitation environment in the arc column is of fundamental importance in emission spectrochemical analysis. The primary purpose for using AgCl in this procedure is to minimize this effect. This type of matrix effect can be estimated by correlations between analytical errors and the excitation potentials and ionization states corresponding to the atomic lines listed in table II. The correlations that are expected to occur from arc theory are discussed in detail in reference 2. However, for purposes of this discussion it is sufficient to indicate that for an arc with a Maxwellian, or nearly Maxwellian, distribution of excitation states, the atomic emission from atoms of the same ionization states and with similar excitation potentials will be similarly affected by excitation matrix effects. Therefore, differences between standard and determined percentages for elements with similar excitation energies should follow the same trend. For example, combinations of elements such as Fe and Mo, V and Nb, and others, which have similar excitation energies can be used to estimate this type of matrix effect.

Comparisons of the data in table IV do not reveal any systematic differences attributable to excitation matrix effects. The differences between the percentages in columns (a) and (c) for the various elements are not well correlated with the excitation energies for the atomic lines listed in table II. Significant differences occurring between results in columns (a) and (c) are believed to be caused by systematic errors in preparing standards from liquid standards. For samples weighing 10 micrograms, differences between the standard (NBS) percentages and column (a) are not systematic and are believed to be caused by long-term drift.

For samples weighing 30 and 100 micrograms, the percentages in columns (a) are systematically lower than the standard percentages. This depression is presumably caused by the increase in the sample-to-diluent ratio. However, the correlations that would be expected in the case of excitation matrix effects are, again, not apparent. The cause of this systematic depression with increasing sample weight is not known. For the 30- and 100-microgram samples, the results of columns (b) and (c) are more accurate

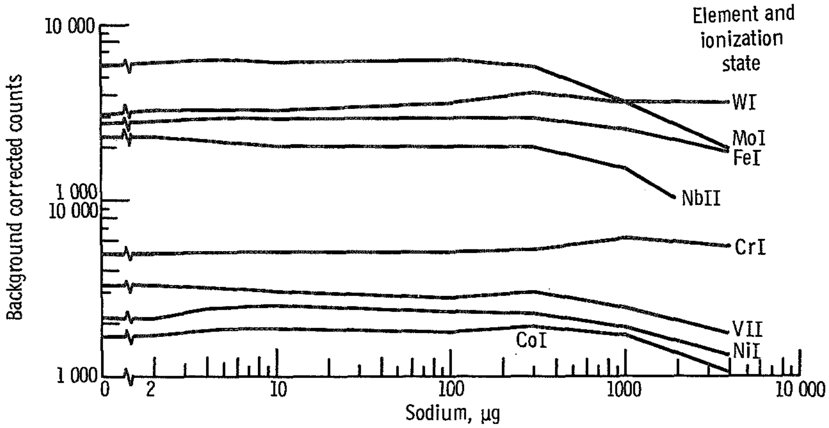

Figure 6. - Effect of sodium on atomic emission of representative elements. Atmosphere, argon; pressure, 350 torr; sample, 1-microgram analyte element with 4 milligrams silver chloride.

than results in column (a) because of the compensations made for lack of quantitative mass recovery and matrix effects in columns (b) and (c), respectively.

Additional corroboration of the negligible excitation matrix effect is shown by the results of figure 6. The effect of increasing amounts of sodium on the emission of 1-microgram amounts of 10 representative elements is shown. The relative emission intensities of these elements is not significantly affected until the sodium-to-element ratio is between 400 and 1000. Because of its lower ionization potential, sodium atoms are expected to have a greater effect on emitted intensities than any of the programmed analyte elements. Therefore, it is improbable that excitation matrix effects are significant in the analysis of sample residues weighing 10 micrograms.

CONCLUDING REMARKS

With the single analytical procedure described herein, samples of unknown compositions can be rapidly analyzed without use of comparison standards. This extends the usefulness of emission spectroscopy to many samples which are not economically analyzed by the comparison-standard technique because of the effort required to develop specific procedures and validate analytical results. The applicability of the procedure to microgram-weight samples is especially advantageous for analysis of deposits, surface films, and other miscellaneous samples derived from various research facilities. The provision for calculating mass balances and the method for correcting spectral interferences are essential for analysis of samples with unknown compositions.

The difficulty of dissolving some samples in acid media can be a limitation of the procedure. However, the experimental results of figure 5 suggest that materials not readily soluble in acids can be analyzed by dissolving them by means of fusions.

The direct-reading spectrometer records the readout of all 20 programmed elements for every sample analyzed. Because of the large amount of data produced, and because of the calculations that are necessary for spectral line interference corrections, automatic data aquisition and computer processing of data are necessary to take maximum advantage of this procedure.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 9, 1969,
129-03.

APPENDIX - SAMPLE VAPORIZATION AND ANODE CONFIGURATION

For the quantitative determination of microgram constituents with a direct-current arc, the quantitative vaporization of analyte elements from the anode is essential. In the procedure described herein, the sample residues are primarily metal halides because of the use of HF and HCl in the dissolution of samples. Therefore, the volatility of the samples is in the temperature range of the various metal halides. The boiling points of the halides that can be formed range from -86° C (SiF_4), 17.5° C (WF_6), 35° C (MoF_6), and 47° C (ReF_6) on the low-temperature end to 1291° C (AlF_3) and 1400° C (TiF_3) on the high-temperature end, with the boiling points of chlorides falling in between those of the fluorides. The boiling point of AgCl is 1550° C. Therefore, the halides of the analyte elements are totally vaporized before the AgCl common matrix. During the arcing cycle, the temperature of the carbon anode increases from ambient temperature to a maximum of about 2800° C at the anode tip. This high temperature ensures total vaporization of AgCl and halide residues.

Of the volatile halides, only Si is lost by volatilization either when drying at 90° C or in evacuation of the arc chamber. Apparently, the vapor pressures of the hydrated halides, formed at the drying temperature of 90° C, are considerably lower than the anhydrous salts. As a result, the vaporization losses that might be expected considering boiling points alone do not occur.

A potential source of error during vaporization of samples in the argon arc is the formation of metal carbides resulting from contact of sample residues with carbon or graphite anodes at temperatures to about 2800° C. This results in incomplete and nonrepeatable vaporizations of samples from the anode. An equally important consideration is the disturbing influence of the vapor streams on the arc column stability in the region near the anode. Spatial stability near the anode is especially important because the analysis line intensities are derived from this region. Although the Ta-tipped cathode eliminates spatial movement of the cathode region and of the arc column proper, spatial movement caused by sample vapor limits the maximum rate of sample vaporization.

The problems of sample vaporization and anode stability were studied and the pointed carbon anode configuration was developed with the AgCl and sample residue contained in the carbon matrix. With this anode-sample system, sample residues are totally vaporized from the anode without disturbing the spatial stability near the anode.

Reactions between the metal halides and the electrodes are minimized by use of carbon electrodes and by intimate contact of the sample with AgCl. The high halide activity in the sample environment effectively retards carbide formation and promotes quantitative vaporization of the metal halides. An example of the effectiveness of this electrode system is the case of tungsten (W). When the liquid sample was placed in a cupped graphite anode and the AgCl was added to the cup as a powder, the recovery of W on the first arcing was about 40 percent of the total recovered on subsequent additions of AgCl and re-arcings. This compares with recoveries of about 97 percent on the first arcing using the carbon anode with AgCl precipitated in the carbon matrix. With the improvement in recovery, the repeatability of tungsten emission improved from 25 percent to about 3 percent, relative standard deviation. Recoveries of carbide-forming analyte elements from graphite electrodes were always unsatisfactory. Diffraction patterns of arced electrodes did not reveal the reason for this, and no explanation can be offered for the differences observed between graphite and carbon electrodes.

In addition to providing quantitative recoveries of the elements, the carbon anode configuration is important in achieving good spatial stability of the anode spot during sample vaporization. The pointed anode results in a stable anode attachment after the first few seconds following spark ignition of the arc. The conical tip provides the variable anode attachment area that is necessary to achieve good stability over the current range from 11 to 36 amperes. The 90° angle at the apex is approximately the optimum angle. Angles of the apex larger that 90° result in less reliable attachment of the anode spot to the electrode tip. With larger angles, the arc can more easily strike to the edge at the juncture between the conical tip and the cylindrical portion of the electrode. Angles at an apex smaller than 90° result in reduced line intensities because the vaporization of the sample tends to be normal to the surface of the cone. All forms of cupped electrodes were also found to be unsatisfactory because of nonrepeatable attachment of the anode spot to a specific location on the anode.

With the anode configuration and the arcing procedures that are specified, no matrix effects have been observed which can be attributed to chemical reactions on the anode.

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