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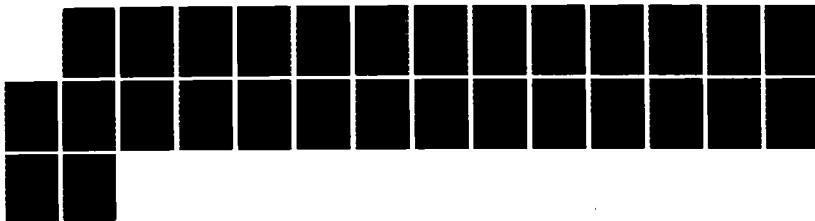
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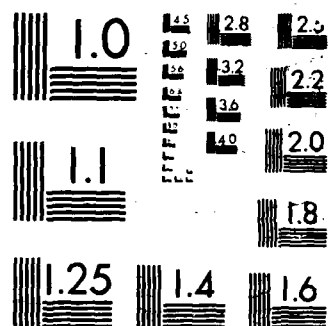
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Quantitative Analysis of the TWT Cathode Impregnants Using Flame Emission Spectroscopy

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30 January 1987

Prepared for
SPACE DIVISION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
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This report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-85-C-0086 with the Space Division, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009-2960. It was reviewed and approved for The Aerospace Corporation by S. Feuerstein, Director, Chemistry and Physics Laboratory.

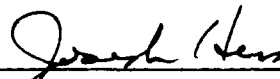
Lt Charles T. Whitson/CGX was the project officer for the Mission-Oriented Investigation and Experimentation (MOIE) Program.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.



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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER SD-TR-86-93		2. GOVT ACCESSION NO. AD-A176 293		3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) QUANTITATIVE ANALYSIS OF TWT CATHODE IMPREGNANTS USING FLAME EMISSION SPECTROSCOPY				5. TYPE OF REPORT & PERIOD COVERED	
				6. PERFORMING ORG. REPORT NUMBER TR-0086(6945-02)-3	
7. AUTHOR(s) Russell A. Lipeles				8. CONTRACT OR GRANT NUMBER(s) F04701-85-C-0086	
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Aerospace Corporation El Segundo, Calif. 90245				10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
11. CONTROLLING OFFICE NAME AND ADDRESS Space Division Los Angeles Air Force Station Los Angeles, Calif. 90009-2960				12. REPORT DATE 30 January 1987	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)				13. NUMBER OF PAGES 25	
				15. SECURITY CLASS. (of this report) Unclassified	
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE					
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.					
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)					
18. SUPPLEMENTARY NOTES					
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Aluminum Barium Barium calcium aluminate dispenser cathode impregnants Barium calcium aluminum analyses					
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Flame emission spectroscopy (FES) is demonstrated for the determination of barium, calcium, and aluminum concentrations in barium calcium aluminate dispenser cathode impregnants. The procedure consists of dissolving the impregnant in 0.5M to 2M hydrochloric acid and analyzing the solution for all three metals by means of a nitrous oxide/acetylene flame. No significant interferences were observed on the basis of the analysis of barium, calcium, and aluminum solution mixtures of known concentration. We found					

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19. KEY WORDS (Continued)

Calcium
Flame emission spectroscopy
Impregnant processing
Traveling-wave tube dispenser cathodes

20. ABSTRACT (Continued)

that the barium, calcium, and aluminum analyses were accurate to $\pm 1.1\%$, $\pm 1.8\%$, and $\pm 1.3\%$, respectively. The method was used to analyze a large number of cathode impregnants. On the basis of these data, significant variations in composition were observed during the processing. Thus, FES is sufficiently sensitive and accurate to detect impregnant compositional variations.

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PREFACE

The author wishes to thank R. Bauer, M. B. Tueling, N. Lum, and D. Coleman for preparation of FES samples; J. Shepherd for useful discussions; and P. A. Adams for the expert operation and maintenance of the FES.

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I. INTRODUCTION

The analysis of barium calcium aluminate impregnants is required to assure uniform impregnant composition during manufacture. Variations in impregnant composition from cathode to cathode can produce variations of barium coverage on the cathode surface, resulting in emission current variations and premature cathode degradation. A precise, accurate, rapid, and simple method is needed to analyze barium, calcium, and aluminum concentrations in cathode impregnants.

In this report we show that flame emission spectroscopy (FES) can be used successfully for barium calcium aluminate impregnant analysis. FES analysis requires minimal sample preparation and only a few minutes to measure the emission from the elements of interest. FES analysis is accurate to between 1 to 2 percent. A wide dynamic range in detection sensitivity, from parts per million to bulk concentrations, can be accomplished by simple dilution. FES techniques are mature, instrumental parameters are fairly well known, and the instrumentation is widely available. Furthermore, interferences between metals are well understood and can easily be suppressed.

We describe a procedure for FES analysis of barium, calcium, and aluminum in barium calcium aluminate dispenser cathode impregnants. Results from the analysis of a large number of impregnants illustrate that current impregnant manufacturing processes are inherently irreproducible. For this reason, monitoring of impregnant composition during manufacture is required.

II. EXPERIMENTAL DESCRIPTION

In this section we provide a brief description of our instrument, the purity of the reagents used, and a description of impregnant and FES sample preparation.

A. INSTRUMENTATION

An Instrumentation Laboratory, Inc. model 251 atomic absorption/emission double-beam spectrophotometer was used for FES analysis. The model 24036-01 burner head was used for the nitrous oxide/acetylene flame. The operating conditions of the spectrometer are listed in Table 1.

B. REAGENTS

Baker ULTREX grade or ACS reagent grade HCl was used to dissolve the impregnants. Deionized water (18 Mohm/cm) was used in all solutions. Commercially prepared 1000-ppm solutions of barium, calcium, and aluminum were used to prepare standard solutions for calibration of the instrument. All other chemicals used were ACS reagent grade.

C. SAMPLE PREPARATION

The barium calcium aluminates were prepared from Mallencrodt reagent grade BaCO_3 , CaCO_3 , and Linde-B Al_2O_3 . 50-g lots of material were processed according to an improved wet mixing procedure based on the Philips-Emet procedure outlined in Fig. 1.¹

The "dry" mixing procedure consisted of the following steps:²

1. The starting materials were milled in a dry 000-size Burundum ball mill jar with 7 to 10 Burundum cylinders for 24 hr to grind the powders.
2. A slurry of the milled powders was prepared in a beaker with about 30 ml of water.
3. About one fifth of the slurry was placed in a high-density, high-purity alumina boat and dried at 130°C prior to calcining at 1350°C for 3 hr.

Table 1. Operating Conditions for the Flame Emission Spectrometer

Element	Wavelength, nm	Slit Width, nm	Burner Height, mm	Burner Orientation, deg.	Red Feather Height, mm	Multiplier Voltage, V
Al	396.1	160	9	0	20	460-530
Ba	553.6	160	11	90	10	530-620
Ca	422.7	80	8	0, (90)	20	460
W	400.9	40	9	0	25	800

Element	Linear Ranges*		Average Error	Linear Correlation**		
	Min	Max		Al	Ba	Ca
Al	0.5	- 10 ppm	1.3%	+1.0	-0.3	+0.6
Ba	0.5	- 30 ppm	1.1%	+0.3	+1.0	+0.9
Ca	0.2	- 2 ppm	1.8%	-0.8	-0.8	+1.0

*See Tables 2 and 3 for range data.

**See Table 3 for detailed linear fits and linear correlation coefficients; + = enhancer; - = suppressor.

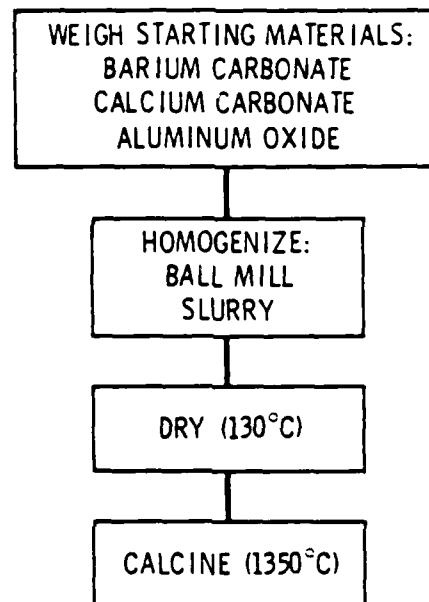


Fig. 1. The Philips-Emet Procedure for Synthesizing Barium Calcium Aluminate Dispenser Cathode Impregnants

The dry procedure was improved by adding a wet mixing step. During wet mixing in a water slurry, more homogeneous impregnants are made because there is better mixing of the starting materials and higher reactivity of the hydrated powders during calcination. The wet or slurry mixing procedure consisted of the following steps:²

1. The starting materials were milled in a dry Burundum ball mill jar for at least 20 hr to grind the powders.
2. About 30 ml of high-resistivity water were added and the slurry was milled for at least 2 hr.
3. The slurry was dried in the ball mill jar at 120°C.
4. Step 2 was repeated.
5. The slurry was placed in a high-density, high-purity alumina boat and dried at 120°C prior to calcining at 1350° for 3 hr.

Aqueous solutions of the barium calcium aluminates were typically prepared by dissolving several milligrams of impregnant in 0.5 to 10M HCl. These solutions were diluted to an approximate concentration of 3 to 5 ppm aluminum and 0.5 to 2M HCl. Nalgene flasks were used for all solutions to be analyzed for aluminum. The use of glass volumetric flasks resulted in irreproducible aluminum measurements because of leaching of aluminum from the glass and adsorption of aluminum on the glass.

In the cases where impregnant from cathodes was analyzed, the cathode button was removed from the heater and was extracted with two to four aliquots of 0.5 to 2M HCl. An ultrasonic bath was used to assure reproducible extraction and to reduce the extraction time.

III. RESULTS

The limits of accuracy are estimated on the basis of analysis of known solutions of barium, calcium, and aluminum. The accuracy is primarily limited by the stability of the flame and background drift. As a demonstration of FES, a large number of barium calcium aluminate impregnants were analyzed. An extension of the analytical method to include impregnants extracted from dispenser cathodes showed variations in impregnant composition in the cathode pores.

A. ACCURACY

The accuracy of FES can be limited by interferences among elements in a sample. The following typical interferences in FES were addressed during the development of this analytical procedure: overlap of spectral bands, the formation of refractory compounds in the flame, and the self-absorption and ionization of elements. The overlap of spectral bands was avoided by the careful selection of bands for analysis. The formation of refractory compounds was avoided by the use of a hot nitrous oxide/acetylene flame. Self-absorption could be minimized in analyzing high concentrations of barium or calcium in the solution by rotating the burner to decrease the optical path-length in the flame. Also, alkaline-earth elements can ionize in the flame, reducing the intensity of neutral excited-state transitions and lowering sensitivity; the ionization of barium and calcium in the flame was suppressed by including a large excess of potassium in the solution.

The accuracy of barium, calcium, and aluminum analyses was determined by analyzing known concentrations of these elements; linear correlations between the elements were examined for evidence of interferences. On the basis of the data in Table 2, the accuracies of the barium, calcium, and aluminum analyses were $\pm 1.1\%$, $\pm 1.8\%$, and $\pm 1.3\%$, respectively.

Because the accuracy of the analysis may be affected by the presence of tungsten in impregnants extracted from tungsten cathodes, the effect of tungsten on the analysis was measured and summarized in Table 2. No

Table 2. Spectral Interferences Due to Barium, Calcium, Aluminum, and Tungsten

Expected Values, ppm			Measured Values, ppm		
Ba	Ca	Al	Ba	Ca	Al
30.0	0	0	28.8	0.01	-
25.0	0	0	24.8	0.01	-
20.0	0	0	20.4	0.01	-
15.0	0	0	15.0	0.02	-
10.0	0	0	9.97	-0.01	-
5.00	0	0	4.94	-0.01	-
1.00	0	0	1.00	-	-
0.50	0	0	0.50	-	-
0.10	0	0	(0.13)	-	-

Average Error:

1.1%

Expected Values, ppm			Measured Values, ppm		
Ba	Ca	Al	Ba	Ca	Al
0	5.00	0	0.02	(3.97)	-
0	4.00	0	0.01	(3.35)	-
0	3.00	0	0.02	(2.65)	-
0	2.00	0	0.01	1.93	-
0	1.00	0	0.02	1.00	-
0	0.50	0	0.01	0.51	-
0	0.10	0	0.01	(0.14)	-

Average Error:

1.8%

Table 2. Spectral Interferences Due to Barium, Calcium, Aluminum, and Tungsten (Continued)

Expected Values, ppm			Measured Values, ppm		
Ba	Ca	Al	Ba	Ca	Al
0	0	10.0	0.00	0.00	9.89
0	0	6.00	0.02	-0.01	6.19
0	0	5.00	-0.02	0.00	5.17
0	0	4.00	0.01	0.01	3.98
0	0	2.00	-	0.02	2.00
0	0	1.00	0.02	-0.01	1.00
0	0	0.50	0.02	0.02	0.52
0	0	0.10	-0.01	0.02	(0.24)
Average Error:			1.3%		

Expected Values, ppm				Measured Values, ppm		
W	Ba	Ca	Al	Ba	Ca	Al
30	0	0	0	-0.05	-0.02	-
20	0	0	0	-0.04	-0.02	-
10	0	0	0	-0.02	0.03	0.13
5	0	0	0	0.07	-0.01	0.12
1	0	0	0	-0.04	0.07	-0.13
0.5	0	0	0	-0.01	-0.01	0.11
Average:				-0.02	0.01	0.06
Standard Deviation:				±0.04	±0.03	±0.12

systematic spectral interference of tungsten on barium, calcium, or aluminum analysis was expected or observed.

The effects of interference between barium, calcium, and aluminum were analyzed by using the data in Table 3. When aluminum was varied and barium and calcium were held constant, a slight suppression of the calcium intensity as a result of aluminum was observed, as shown by the linear fit and the linear correlation coefficient, r , near -1 (Ref. 2). This previously reported effect³ was found to be due to the formation of refractory calcium aluminates that are not completely dissociated in the flame. When barium and aluminum were held constant and calcium was varied, enhancement of the barium signal with increasing calcium was observed. The apparent enhancement is due to a calcium molecular emission line very near the barium line.⁴ When calcium and aluminum were held constant and barium was varied, no significant correlations due to interferences were observed. Generally, interference between elements can increase the variation in the measured value of an element by up to $\pm 5.0\%$. This error can be eliminated by using a calibration standard that closely matches the expected composition of the samples.

B. ANALYSIS OF IMPREGNANT POWDERS

Variations in impregnant composition as a result of processing were determined by examining a wide range of impregnant compositions made in our laboratory according to the wet mixing procedure in Section II.C. The results of the analyses of 4:0.5:1, 4:1:1, 5:3:2, and 5:2:2 impregnants are presented in Table 4. In general, these impregnants show a wider variation (4.3 to 11.6% average deviation) in calcium and aluminum than would be expected on the basis of the inherent accuracy of the FES technique (1.1 to 1.8%). In particular, a large variation in the formulation of 4:0.5:1 was observed, indicating problems with the initial mixing homogeneity and with the incorporation of calcium and aluminum into the impregnant. The average deviations observed in the remaining impregnants indicate that about a 5% variation is typical of the wet-mixed materials used in this study. Thus, the results of FES analysis have shown that the mixing procedure can be controlled by FES, which has an accuracy of about 1.5 to 2%.

Table 3. Chemical Interferences Due to Barium, Calcium, and Aluminum

Expected Values, ppm			Measured Values, ppm		
Ba	Ca	Al	Ba	Ca	Al
20	2	9	20.38	1.83	8.74
20	2	7	20.59	1.81	6.95
20	2	5	19.75	1.92	5.00
20	2	3	20.33	1.92	3.15
20	2	1	18.83	1.99	-
Average:			19.98	1.89	
Standard Deviation:			±0.2%	±3.9%	

Correlations:

$$[\text{Ba}] = 19.94 + 0.054[\text{Al}]$$

$$r = +0.365$$

$$[\text{Ca}] = 1.99 - 0.021[\text{Al}]$$

$$r = -0.849$$

$$[\text{Al}] = -0.366 + 1.07[\text{Al}]$$

$$r = 1.000$$

Expected Values, ppm			Measured Values, ppm		
Ba	Ca	Al	Ba	Ca	Al
20	3	5	19.96	(2.76)	4.84
20	2	5	19.87	2.03	4.76
20	1	5	19.49	1.02	4.86
20	0.5	5	18.91	0.50	4.58
20	0.2	5	18.64	0.18	4.68
Average:			19.37		4.74
Standard Deviation:			+3.0%		+2.4%

Correlations:

$$[\text{Ba}] = 18.7 + 0.513[\text{Ca}]$$

$$r = 0.948$$

$$[\text{Ca}] = 0.016 + 0.975[\text{Ca}]$$

$$r = 1.000$$

$$[\text{Al}] = 4.65 + 0.069[\text{Ca}]$$

$$r = 0.644$$

Table 3. Chemical Interferences Due to Barium, Calcium,
and Aluminum (Continued)

Expected Values, ppm			Measured Values, ppm		
Ba	Ca	Al	Ba	Ca	Al
50	2	5	46.03	1.94	4.37
30	2	5	29.45	2.00	5.03
20	2	5	18.84	2.01	4.66
10	2	5	-	1.94	4.64
5	2	5	5.11	2.00	4.65
Average:				1.98	4.67
Standard Deviation:				+1.8%	+5.0%

Correlations:

$[Ba] = -0.877 + 1.09[Ba]$	$r = 0.999$
$[Ca] = 2.02 - 0.002[Ba]$	$r = -0.802$
$[Al] = 4.80 - 0.005[Ba]$	$r = -0.302$

Table 4. FES Analysis of Impregnant Powders

Mole Ratio				Weight Percent			Weight Discrepancy, %
BaO	CaO	Al ₂ O ₃		Ba	Ca	Al	
4	: 0.50:	1		73.9	2.7	7.3	-
3.97:	0.61:	0.99		73.3	3.3	7.2	5.7
4.08:	0.50:	0.88		75.4	2.7	6.4	11.6
4.17:	0.50:	0.75		77.0	2.7	5.4	7.8
4.22:	0.44:	0.71		77.9	2.4	5.1	3.9
4.02:	0.53:	0.95		74.3	2.9	6.9	5.7
4.06:	0.52:	0.90		75.0	2.8	6.5	5.6
4.09:	0.52:	0.85		75.6	2.8	6.2	1.0
Avg.: 4.09 0.52 0.86				75.5	2.8	6.2	5.9
SD: ±0.09 ±0.05 ±0.10				±2.1%	±9.8	±11.6%	±3.3
4	: 1	: 1		71.2	5.2	7.0	-
4.00:	1.21:	0.88		71.3	6.3	6.2	7.3
3.97:	1.19:	0.94		70.7	6.2	6.6	4.6
Avg.: 3.99: 1.20: 0.91				71.0	6.2	6.4	5.9
SD: ±0.02 ±0.01 ±0.04				±0.6%	±1.2%	±4.6%	±1.9

Table 4. FES Analysis of Impregnant Powders (Continued)

Mole Ratio			Weight Percent			Weight Discrepancy, %
BaO	CaO	Al ₂ O ₃	Ba	Ca	Al	
5	: 3	: 2	60.3	10.6	9.5	-
5.10:	3.11:	1.79	61.4	11.0	8.5	9.5
5.07:	2.98:	1.91	61.1	10.5	9.0	5.8
5.06:	2.93:	1.95	61.0	10.3	9.2	14.5
5.01:	3.16:	1.89	60.4	11.1	9.0	6.6
5.07:	3.11:	1.83	61.2	10.9	8.7	7.1
5.13:	2.79:	1.91	61.9	9.8	9.1	2.6
5.04:	3.13:	1.88	60.7	11.0	8.9	1.9
5.04:	3.28:	1.79	60.8	11.6	8.5	1.2
4.98:	2.94:	2.11	60.1	10.0	10.0	-0.96
5.02:	2.90:	2.02	60.6	10.2	9.6	3.2
4.98:	2.84:	2.11	60.1	10.0	10.0	0.04
5.01:	2.85:	2.07	60.4	10.0	9.8	-1.6
5.04:	2.81:	2.04	60.8	9.9	9.6	1.3
4.98:	2.84:	2.11	60.1	10.0	10.0	0.04
4.95:	2.88:	2.13	59.7	10.1	10.1	2.5
4.95:	3.07:	2.04	59.7	10.8	9.7	12.3
4.98:	2.84:	2.11	60.1	10.0	10.0	0.04
5.05:	2.75:	2.06	61.0	9.7	9.8	0.5
Avg.:	5.03:	2.96: 1.99	60.6	10.5	9.4	3.7
SD:	±0.05	±0.15 ±0.12	±1.0%	±5.1%	±5.9%	±4.6

Table 4. FES Analysis of Impregnant Powders (Continued)

Mole Ratio				Weight Percent			Weight Discrepancy, %
BaO	CaO	Al ₂ O ₃		Ba	Ca	Al	
5	: 2	: 2		63.4	7.4	10.0	-
4.88	: 2.29	: 2.02		61.9	8.5	10.1	4.6
5.09	: 2.00	: 1.87		64.5	7.4	9.3	0.8
5.02	: 2.17	: 1.88		63.7	8.0	9.4	4.8
5.05	: 2.16	: 1.83		64.1	8.0	9.1	1.5
4.96	: 2.13	: 2.03		62.6	7.9	10.1	6.2
5.07	: 2.14	: 1.82		64.3	7.9	9.1	1.4
4.96	: 2.23	: 1.93		63.0	8.3	9.6	3.6
Avg.: 5.00: 2.16: 1.93				63.4	8.0	9.5	3.5
SD: +0.07 +0.09 +0.11				±1.5%	±4.3%	±5.7%	+2.3

C. ANALYSIS OF IMPREGNANTS EXTRACTED FROM CATHODES

The FES technique was used to examine variations in composition that can result during cathode impregnation. The impregnation process consists of melting an impregnant powder in contact with a porous tungsten button. The barium calcium aluminate solid solutions melt first and are drawn into the porous tungsten by capillary action. Because the calcium oxide phase in the impregnant has a higher melting point, this phase melts last and contributes to that portion of the impregnant near the front of the cathode.

This effect is illustrated by the composition of impregnants extracted from cathodes (see Table 5). When impregnant was extracted from the front of intact cathodes, composition was about 5:2.5:2. When cathodes were crushed so that impregnant was analyzed from the entire volume of the cathode, the composition was about 5:2:2. The nominal composition of the initial powder was 5:3:2. This shows that calcium-poor impregnant melted first and the calcium concentration increased as the calcium oxide dissolved.

A concentration profile of the impregnant in a cathode was obtained by multiple extractions of impregnant from the emitting surface of the cathode (see Table 6). These measurements also show the variation in composition that can be caused by incongruent melting of the impregnant. We found that the aluminum concentration decreases toward the center of the cathode (samples 4 through 7) and the calcium concentration is higher toward the front of the cathode (samples 2 through 4). Thus, these data are consistent with an impregnation mechanism whereby a 5:2:2 solid solution initially melts and impregnates the cathode, followed by dissolution of more calcium.

These measurements demonstrate that FES has sufficient sensitivity to obtain concentration profiles by means of extraction. Further work needs to be done to confirm that preferential extraction does not alter the measured concentrations.

Table 5. FES Analysis of Impregnants Extracted from Dispenser Cathodes

Cathode Manufacturer	Mole Ratio			Impregnant Extracted, mg *	Notes
	BaO :	CaO :	Al ₂ O ₃		
Nominal	5	: 3	: 2		
Semicon	5.19	: 2.51	: 1.98	0.94	front extraction;
Semicon	5.40	: 1.88	: 2.02	3.53	6.8 mg impreg. total crushed button;
					6.7 mg total
Spectramat	4.85	: 2.64	: 2.42	0.92	front extraction
Spectramat	5.31	: 2.05	: 2.05	2.96	crushed button

* Impregnants extracted 3 times with about 1 ml of 10-11.9M HCl

Table 6. Effect of Multiple Extractions

Sample	Mole Ratio			Impregnant Extracted, mg	Notes
	BaO	CaO	:Al ₂ O ₃		
Nominal	5	: 3	: 2		Extracted with 2 ml 2M HCl aliquots and diluted up to 50 ml for analysis at 0.5M HCl.
1 - Front	5.03:	2.36:	2.31	0.94	
2	4.82:	3.12:	2.20	0.43	
3	4.87:	2.88:	2.26	0.37	
4	5.01:	3.30:	1.82	0.22	
5	5.16:	2.48:	2.04	0.48	
6	5.21:	2.34:	2.04	0.35	
7	5.34:	2.08:	1.99	0.31	
				3.10	6.0 mg total weight

IV. CONCLUSIONS

Flame emission spectroscopy is a useful analytical method for measuring cathode impregnant composition as well as for controlling impregnant composition during dispenser cathode manufacture. We showed that the barium, calcium, and aluminum analyses are inherently accurate to between 1 and 2%. This accuracy is sufficient for monitoring impregnant composition.

We showed that FES can be used to detect the compositional variation in impregnant powders that results from processing. Cathode impregnants typically show about 5% variation in calcium and aluminum concentrations. We believe this variation in composition is due to inhomogeneous mixing of the starting materials. Furthermore, we found that barium-rich impregnants (e.g., 4:0.5:1) are subject to even greater variations than barium-poor impregnants (e.g., 5:3:2). Thus, monitoring is required to assure lot-to-lot uniformity of composition.

We demonstrated that FES can be used to study the spatial distribution of impregnant composition in dispenser cathodes. Analysis of impregnant fractions extracted from a cathode showed that considerable variation in composition exists within the cathode. Variations in the impregnation process can result in a different distribution of composition and may contribute to irreproducible cathode performance.

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LABORATORY OPERATIONS

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