

## Analysis of Glass and Ceramic Frit by Atomic Absorption Spectrophotometry

SIR: We have used atomic absorption spectrophotometry to good advantage for the determination of a number of elements in glass and ceramic frit. The method is rapid and convenient, since as many as 13 elements (see Table I) can be determined in one solution of the sample, aliquots of which are diluted as needed.

Previously, the alkali and alkaline earth elements had been determined by flame photometry, and established photometric and polarographic methods had been used for the determination of the other elements. Many of the interference problems encountered in the determination of the alkali and alkaline earth elements by flame photometry are also present in atomic absorption, but can be resolved with much less effort. The determination of the other elements is remarkably free from interference effects.

### EXPERIMENTAL

**Apparatus.** Absorption measurements were made with a Perkin-Elmer Model 214 atomic absorption spectrophotometer equipped with an air-acetylene premix burner. The slot in the burner-head is 10 cm. long.

**Reagents.** Strontium Chloride Solution (33 grams of Sr/liter). Dissolve 100 grams of  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  in water in a 1-liter volumetric flask and dilute to volume.

**Procedure.** To a 1-gram sample in a platinum dish were added 10 ml. of HCl, 5 ml. of HF, and, if the sample contained much boron, 10 ml. of methyl alcohol. The solution was evaporated to dry salts. Five milliliters of HCl was added and the solution again was evaporated to dryness; this process was repeated twice. The salts were then dissolved in 100 ml. of HCl (1.2M) with heat, and finally diluted to 200 ml. in a volumetric flask.

Appropriate dilutions of the sample stock solution were prepared according to the sensitivity for the elements being determined (see Table I). These solutions were aspirated into the flame at approximately 4 ml. per minute, accompanied by an appropriate series of single element standard solutions. All solutions contained HCl in 0.6M concentration, and the solutions used for the determination of the alkali and alkaline earth elements contained 5 ml. of the strontium chloride solution per 100 ml.

**Interferences.** No serious interference was encountered for lead, zinc,

manganese, iron, copper, cobalt, and nickel. Strontium chloride was added to overcome the inhibiting effect of such elements as aluminum and phosphorus in the determination of the alkaline earth elements, as suggested by David (1).

The presence of strontium was found not only to slightly enhance the absorption of the alkali elements, but also to minimize the mutual enhancement effect of these elements as shown in Table II. The results in Table II were obtained with the burner head positioned at an angle to allow the beam from the external source to pass through a shorter flame path. This technique was used frequently where both concentration and sensitivity of an element were high. Combined with the use of strontium to suppress interference effects for both the alkali and alkaline earth elements, it permitted the use of single dilution for the determination of several elements.

### RESULTS

National Bureau of Standards glass samples were used to investigate accuracy and precision for many of the elements. In Tables III and IV, the average of 10 determinations is compared with the NBS certificate value for each element. The relative standard deviation for the 10 determinations is also shown. Table V shows a comparison of single atomic absorption values with those obtained by established photometric methods for cobalt, copper, nickel, and manganese oxides in two typical ceramic frit samples.

Table I. Parameters and Sensitivity

Element	Wave-length (Å.)	Mechanical slit width (mm.)	Reciprocal sensitivity (p.p.m./% Å.)
Ba	5536	0.100	10
Ca	4227	0.100	0.06
Co	2407	0.200	0.3
Cu	3247	0.100	0.2
Fe	2483	0.110	0.2
Pb	2833	0.100	0.5
Li	6708	0.360	0.03
Mg	2852	0.100	0.01
Mn	2795	0.100	0.1
Ni	3524.5	0.100	0.7
K	7665	1.000	0.06
Na	5890	0.100	0.01
Zn	2138	0.385	0.05

Table II. Enhancement Effects

Effect of Potassium on Sodium			
Na (p.p.m.)	K (p.p.m.)	Sr (p.p.m.)	Absorbance (5890 Å)
3	0	0	0.166
3	20	0	0.184
3	0	700	0.183
3	20	700	0.184
0	0	700	0.000
0	200	0	0.001
Effect of Sodium on Potassium			
K (p.p.m.)	Na (p.p.m.)	Sr (p.p.m.)	Absorbance (7665 Å)
3	0	0	0.177
3	9	0	0.188
3	0	700	0.200
3	9	700	0.201

Table III. Analysis of NBS 91 (Opal Glass)

	Certificate value (%)	No. of detns.	Av. value detd.	Rel. std. dev.
CaO	10.48	10	10.58	1.2
Na <sub>2</sub> O	8.48	10	8.42	0.5
K <sub>2</sub> O	3.25	10	3.33	0.7
PbO	0.097	10	0.111	1.7
ZnO	0.08	10	0.082	1.5
Fe <sub>2</sub> O <sub>3</sub>	0.081	10	0.083	4.1

Table IV. Analysis of NBS 89 (Pb-Ba Glass)

	Certificate value (%)	No. of detns.	Av. value detd.	Rel. std. dev.
PbO	17.50	10	17.3	1.4
K <sub>2</sub> O	8.40	10	8.30	1.2
Na <sub>2</sub> O	5.70	10	5.76	1.0
BaO	1.40	10	1.39	2.7
CaO	0.21	10	0.21	0.8
MgO	0.03	10	0.025	1.4
MnO	0.088	10	0.088	1.7

Table V. Comparison of Results

	Frit No.1		Frit No.2	
	Photometric	Atomic absorption	Photometric	Atomic absorption
CuO	0.66	0.69	0.15	0.16
CoO	0.30	0.29	1.35	1.37
NiO	1.64	1.63	0.05	0.060
MnO	0.16	0.18	2.29	2.32

## LITERATURE CITED

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## Adsorption of Dimethyldodecylamine Oxide under Polarographic Conditions

SIR: A recent paper on the polarographic behavior of dimethyldodecylamine oxide (DDAO) emphasized the importance of adsorption and micelle formation of the electroactive compound (10). This complements our interest in the quantitative role of similar effects of electroinactive surfactants on polarographic electrode processes (4, 5). However, the electrocapillary drop-time measurements described for DDAO were somewhat unusual with respect to the following observations. The base electrolyte curve appeared more bell-shaped than parabolic (24). For solutions containing DDAO, the experimental points lie outside the electrocapillary curve for the base solution at extreme anodic and cathodic potentials with respect to the potential of zero charge (p.z.c.) of the electrode in the base electrolyte. The difference in drop times ( $\Delta t$ ) at the p.z.c. for additions of  $1.0 \times 10^{-4}$ ,  $1.0 \times 10^{-3}$ , and  $8.0 \times 10^{-3}M$  DDAO corresponds to changes in surface tension ( $\Delta\gamma$ ) of about 190, 217, and 242 dynes/cm., respectively, which are inordinately large values compared with those for the adsorption of a wide variety of organic surface-active materials on mercury (2, 3, 5, 13, 16). The purpose of this communication is to clarify the apparent inconsistencies listed above and to extend on a quantitative basis the work initiated by Chambers (10).

### EXPERIMENTAL

Electrocapillary measurements were recorded by conventional drop-time technique using a Radiometer Model P. O. 4 Polariter. The dropping mercury electrode (DME) for these experiments had a drop-time of 7.290 seconds at the p.z.c. of the base electrolyte, which consisted of an aqueous acetic acid-potassium acetate buffer solution of pH 5.0 and ionic strength of 0.34. Drop-time measurements were made in the absence and presence of varying concentrations of DDAO from a range of  $3.0 \times 10^{-5}$  to  $1.0 \times$

$10^{-2}M$  in the buffer solution. DDAO (99.5% purity) was obtained from the Research Laboratories of Procter and Gamble Co., Cincinnati, Ohio, and dried over  $P_2O_5$  in a vacuum desiccator to remove final traces of water. All other chemicals were of the highest analytical reagent grade and dissolved in equilibrium water prepared as described previously (2, 3). The solutions were deaerated by bubbling nitrogen, which was purified by the vanadous chloride method suggested by Meites (23), and then presaturated with the same acetate buffer solution contained in the polarographic cell. The cell was designed according to one described by Griffiths and Jackman (18), and ingress of oxygen or air during a run was prevented by maintaining a slight, positive pressure of purified nitrogen over the solution. Double-distilled mercury was further purified according to the procedure given by Ives and Janz (20).

For each drop-time measurement, the DME was polarized at a fixed potential relative to a reference electrode (S.C.E.), and at least 30 drops were counted and measured by means of a precision stop watch. The drop times were also confirmed by measurements of capacitative current *vs.* time curves on the P. O. 4 Polariter at a calibrated chart speed. Capacitative current-time (*i-t*) traces on the recorder chart paper show current rise (as a function of time) up to a maximum value ( $<0.05 \mu a.$ ), which decreased instantaneously to zero as the mercury drop fell. Again, at least 30 such (*i-t*) traces were recorded for each fixed potential, and the average distance between two points of zero current was taken as the drop time of the electrode. The manual and automatic (*i-t*) determinations of drop times agreed very well.

Standard polarograms were also measured for several concentrations of DDAO in the same acetate buffer solution used for the electrocapillary studies.

### RESULTS AND DISCUSSION

Attempts to record electrocapillary curves for the adsorption of DDAO on a stationary mercury electrode in a modern Lippman electrocapillarometer

(2, 3) were unsuccessful. DDAO resembles the triton series of polyoxyethylene ether compounds in its strong wetting properties, and no direct, reproducible measurements of surface tension at the mercury-solution interface were possible (5, 14). Previous studies (1, 5, 6, 21) have indicated that under proper conditions surface tension values based on drop-time measurements correspond very closely to those obtained on the Lippman apparatus.

Figure 1 shows a typical set of electrocapillary data for DDAO over a range of +0.1 to -1.1 volts (S.C.E.). The drop times were converted to surface tension units by calibration of our DME with published data for KCl solutions (15) and appropriate corrections were applied according to Corbuser and Gierst (12). Although the manual and automatic recordings of drop times are comparable, the latter method is preferred not only for convenience, but also because the rate of change of capacitative current with time can serve as a useful indication of any unusual or unexpected polarographic behavior. For example, minute accidental plugging of the electrode capillary caused small kinks to be observed on the (*i-t*) plots, which led to erratic drop-time measurements. This was verified by the regular flow of mercury and faithful reproduction of standardized drop times when the same DME was replaced after rigorous cleaning of the glass capillary. DDAO and other highly surface-active materials can inadvertently contaminate the internal surface of the capillary tubing by adsorption on glass (6, 14).

The results in Figure 1 are radically different from those reported by Chambers, not only for the base electrolyte but also for other solutions containing comparable concentrations of added DDAO. It is possible that our drop time *vs.* potential curves are more correct because of their conventional form and the apparent care reported in taking the measurements. The most