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The Separation Kinetics and Determination of Transition and Representative Metal Contaminants from Chlor-Alkali Cell Mercury with Ammonium Hydroxide Extraction and X-Ray Fluorescence

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NOTE

The Separation Kinetics and Determination of Transition and Representative Metal Contaminants from Chlor-Alkali Cell Mercury with Ammonium Hydroxide Extraction and X-Ray Fluorescence

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Abstract

The chemical separation of transition and representative metal contaminants, e.g., Fe, Ni, Zn, and Mo, from industrial chlor-alkali cell mercury is described using ammonium hydroxide as an extractant with subsequent determination of the extracted oxides by x-ray fluorescence.

INTRODUCTION

The existence of mercury contamination by nonalkali metals has plagued the chlorine industry since the start-up of the first Castner rocking mercury cell plant in the early 1900s. Till the present time, no process has been satisfactory for removing and analyzing these foreign materials (*1*, *2*).

Iron, nickel, zinc, and molybdenum frequently occur as contaminants in the used cathodic mercury. The concentrations of these metals should be determined on a routine basis. They generally remain at levels below 300 ppm in the fluid mercury.

After an extractive chemical separation of the metal contaminants from

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a sample of used mercury with 30% ammonium hydroxide, the mixed oxide–hydroxide solute is filtered from the boiled-down aqueous solvent onto a Celite filter pad. The metal–Celite mixture is dried, blended, and determined by an x-ray fluorescence scanning technique. The detection limit is less than 1 ppm for each metal relative to the mass of the mercury.

After extraction with ammonium hydroxide, the metals may be determined by other methods, such as optical spectrometry. Although the optical methods provide accurate analyses of these metals at the ppm level, the many operations involved preclude rapid analysis. By using the x-ray fluorescence method presented here, an experienced operator can conveniently run 12 mercury sample analyses in an 8-hr day (*3*).

EXPERIMENTAL

Sample Preparation

A 100-ml sample of used chlor-alkali cell mercury is extracted with multiple 400 ml portions of ammonium hydroxide till a clear aqueous phase persists. Each extraction is stirred not less than 20 min nor more than 90 min. Longer extraction times result in some loss of mercury, and the shorter times are not adequate for removing the contaminant metals as shown by the kinetic data in Fig. 1.

A special square stirring reactor is used in conjunction with a high-speed stirring motor. The combined volume of all the ammonium hydroxide extractions is boiled down to 20% of its initial volume, and the sample is then cooled to room temperature. A Celite filter pad is prepared in a 3-in. Buchner funnel fitted with one sheet of Whatman No. 40 filter paper. This involves about 3 g of filter aid. The samples are filtered, washed with water, and dried at 100°C under a vacuum for about 30 min.

The dry sample of Celite plus metals is weighed, then homogenized in a Spex Industries Mixer Mill No. 8000 or other high-speed shaker. The sample is now in a well-blended and desirable form for analysis by x-ray fluorescence.

Instrumental Method

Standard samples are prepared to contain the most stable iron, nickel, zinc, molybdenum, etc. oxides in concentrations from 0 to 2%, depending on the metal, by mixing reagent-grade iron oxide (Fe_2O_3), nickel oxide

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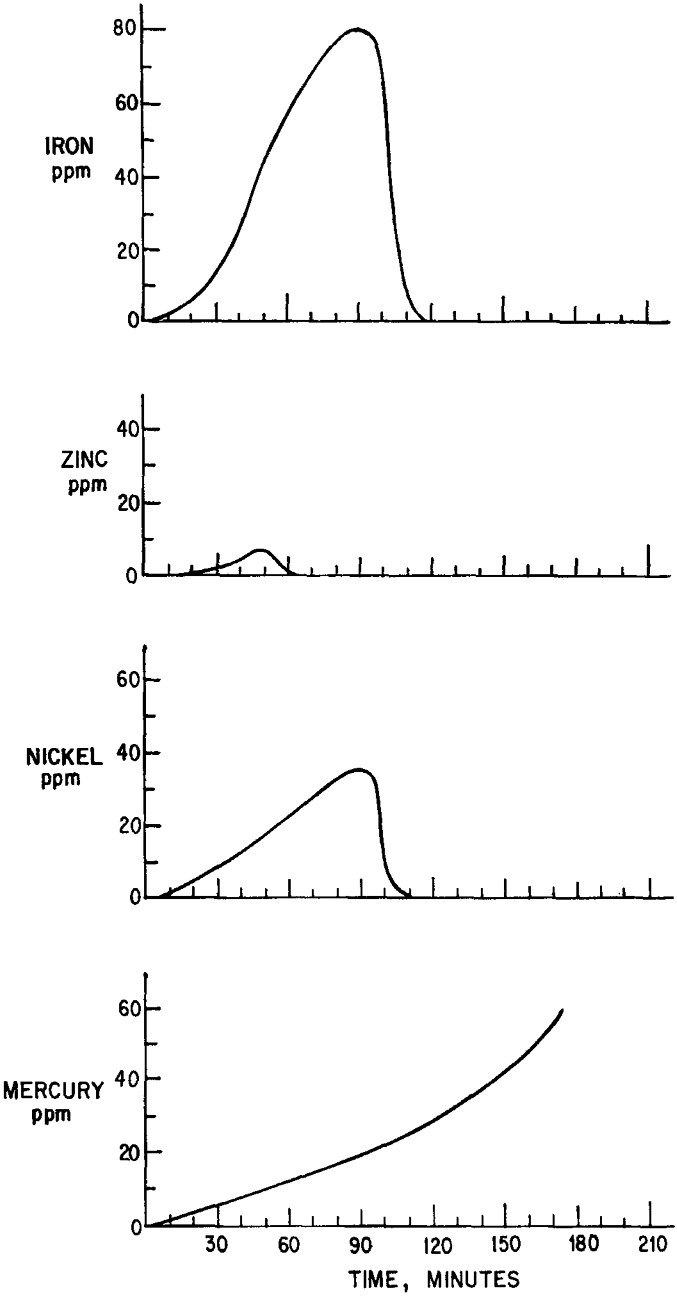

FIG. 1. Kinetic data for the relative extraction rates of iron, zinc, nickel, and mercury from a typical cathodic mercury sample using ammonium hydroxide as an extractant.

(NiO), zinc oxide (ZnO), and sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) with high-purity Celite.

The apparatus used is a Norelco Vacuum X-ray Spectrograph with a Norelco circuit panel and other usual accessory equipment. The instrument settings and conditions are shown in Table 1.

The x-ray sample holders are commercially available cylindrical stainless steel cups. Each has a 0.25-mil window of Mylar film as a bottom. The powdered oxide–Celite samples are placed into the cells to a minimum depth of 0.75 in. because any additional sample thickness has no effect on the results. The cells are cleaned and dried after use, and a new Mylar window is used for each new sample.

This procedure utilizes a scanning technique where the instrument settings are constant for all of the elements (*4*). The x-ray intensities for each element are determined by measuring the peak height in scale divisions at each of the respective 2θ angles. The first order K_α lines are used in all cases, and the background corrections made by scanning approximately 1° – 2θ away from the peak angle (*5*). In order to reduce the scanning time, only small regions are scanned for each element. A standard attenuation is chosen for each element to simplify the procedure. The regions scanned and the corresponding standard attenuations are shown in Table 2.

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TABLE 1

X-Ray Instrumental Conditions

Primary x-ray source	FA-60 tube, tungsten target
Generator	50 kV constant potential
Excitation	45 kV, 30 mA
Counter	Scintillation
Crystal	Lithium fluoride; $2d = 4.028$ Å
Scanning speed	1° – 2θ/min
Atmosphere	Helium
PHA, Baseline	6 V
Window	Integral position

TABLE 2

Angular Regions Scanned

Element	Region scanned 2θ°	Attenuation
Mo	18 to 22	8 × 16 × 1
Zn	40 to 43	8 × 8 × 1
Ni	47 to 50	8 × 8 × 1
Fe	56 to 59	8 × 4 × 1

Calibration curves are prepared of net peak height in scale divisions versus the percentage of the element per gram of Celite. While an analysis is being performed using these curves, the instrumental drift is corrected by varying the current on the x-ray source until the standards give intensities on which the calibration curve is based.

RESULTS AND DISCUSSION

For each element a slight bend in the calibration curve is obtained at the higher concentration levels, thus indicating some matrix and interelement effects. As shown in Table 3, the peak heights for the elements are great enough to permit a further dilution of the sample with Celite, and this step has been shown to reduce the matrix and interelement effects significantly (*6*).

In order to obtain a value for the precision of this x-ray method, a series of eight Celite sample blends with various metal concentrations was analyzed by x-ray and then by an optical emission spectrometric method. The comparative results are shown in Table 4. The accuracy of the x-ray method could undoubtedly be improved by rigid control of particle size and packing of the material in the sample holder, and also by use of slower scanning rates. The results quoted are, however, more than sufficiently accurate for routine control purposes, especially after computing the metals concentrations based on the large mass of mercury sampled.

The data for calculating these analytical concentrations are determined from the chart scans. The spectral peak heights are determined in net scale divisions. The net chart divisions are converted into the percentage of metal in Celite by referring them to an analytical curve, then using an equation derived from the curve. The metal concentrations in the Celite

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TABLE 3

Net Scale Divisions at Various Concentrations

Element	% Conc in Celite	Net scale divisions
Mo	0.02	18
	0.10	71
Zn	0.18	18
	1.76	80
Ni	0.07	16
	1.97	220
Fe	0.33	29
	1.99	128

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TABLE 4

Comparison of Methods (% in Celite)

	% Ni		% Fe		% Mo		% Zn	
Sample	X-ray	Optical	X-ray	Optical	X-ray	Optical	X-ray	Optical
1	0.60	0.54	2.3	2.6	0.031	0.024	0.070	0.060
2	0.39	0.40	2.0	1.9	0.008	0.007	0.043	0.034
3	0.29	0.28	1.0	1.2	0.006	0.005	0.039	0.030
4	0.98	1.02	3.9	3.9	0.024	0.023	0.105	0.100
5	0.52	0.46	1.9	1.9	0.014	0.014	0.031	0.036
6	0.56	0.52	1.9	2.1	0.008	0.010	0.074	0.063
7	0.53	0.46	1.7	1.9	0.007	0.010	0.060	0.060
8	0.54	0.46	2.0	1.8	0.010	0.009	0.070	0.060

are referred to the initial metal concentrations in the mercury by using the relation:

$$\text{ppm metal in mercury} = \frac{\%\ \text{metal in Celite} \times \text{grams of Celite} \times 10^4}{\text{grams of mercury}}$$

SUMMARY

The presently outlined process for the extraction and analysis of the nonalkali metal contaminants in industrial chlor-alkali cell mercury utilizes such a large weight of sample (mercury) that a typical analysis will yield results in the range of one part in a million by weight. There is a time dependence for the amount of metal removed from the contaminated mercury with the ammonium hydroxide. The amount of stirring must be sufficient for the complete liberation of the foreign metals from the host media, but of short enough duration that significant amounts of the mercury are not lost, as observed in the kinetic data in Fig. 1.

The precision and accuracy of the determination for iron, nickel, zinc, and molybdenum by the x-ray method described herein are considered to be very satisfactory. Many other metals which are commonly found in electrolytic mercury may be determined in the same manner, i.e., Pb, Cu, Cd, Co, Mn, Sn, Cr, Ti, and V (*3*).

In comparison to methods used previously, the x-ray method provides improvement in speed, and sample preparation is much less troublesome. An experienced operator can prepare and analyze 12 or more cell samples in an 8-hr day, and the analytical precision and accuracy is as good as in the optical methods.

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