Preparation of Ash and Spectrochemical Determination of Traces of Metallic Elements in Oils, Fats, and Related Substances*

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EMISSION spectrographic techniques offer means for the determination of traces of metallic elements in fats and oils. Successful application of them should be of particular interest in researches on the effect of traces of such elements on stability and on the measurement of metallic contamination obtained from processing equipment or resulting from incomplete removal of hydrogenation catalysts. Markley and Goss (1) have commented that "In view of the fact that a few parts per million of copper salts (oleate) adversely affect the stability or keeping quality of most refined oils, it would be of interest to know how much of the total copper, contained in soybeans, finds its way into the refined oil." Lea (2) showed the extremely small concentrations of many metals which may affect the keeping quality of oils.

As the amount of ash and, consequently, of any of the metallic elements present in fats and oils is very small, a preliminary preparation of the sample by special ashing methods is essential in order that the full amount may be recovered and at the same time the organic matter may be eliminated by combustion. The purpose of the present communication is to describe an ashing procedure that has proved adequate and to discuss briefly some features of the spectroscopic techniques involved in making the essential measurements.

Preparation of the Sample and Standards

A modification of the magnesium-nitrate method, widely used for the ashing of samples of organic materials for the determination of phosphorus, was found satisfactory and was adopted.

A sample of exactly 2.5 gm. of the fat or oil is accurately weighed into a 100-ml. Vycor dish (90 mm. across the top) and 5 ml. of an alcoholic solution of magnesium nitrate [250 gm. $Mg(NO_3)_2 \cdot 6H_2O$ per liter of 95% C_2H_5OH] is added. The dish is covered with an inverted short-stemmed Pyrex funnel, whose maximum diameter is less than the maximum diameter of the dish. The sample is heated on a hot plate and the temperature gradually and cautiously raised until fuming occurs. When the fuming has ceased, the temperature is again raised gradually until the maximum temperature of the hot plate, approximately 300° C., is attained and heating is prolonged for at least an additional 30 minutes. The charred sample is cooled and a solution of the selected internal standard is added. The sample is then dried overnight in a vacuum desiccator over P_2O_5 or an equally efficient desiccant. The dried sample is then ashed in a muffle furnace, with an initial temperature of 225° C. and increasing in increments of 25° C. at 30-minute intervals until a temperature of 450° C. is reached. The samples are held at this temperature in the muffle furnace overnight and then cooled and quantitatively transferred to a small mortar with the aid of a camel-hair brush. The ash is then finely ground, very thoroughly mixed, and transferred to a weighing bottle for storage.

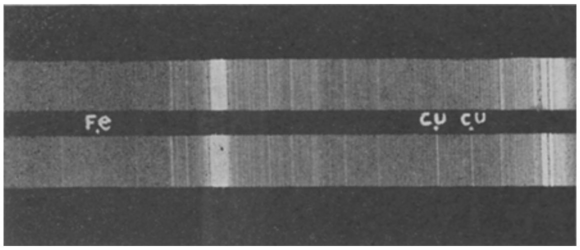

FIG. 1. Spectra of molecularly distilled oil ashed in Vycor dish (upper spectrogram) and in porcelain dish (lower spectrogram).

Certain precautions must be observed. The magnesium nitrate used must be entirely free of the metallic elements to be determined. Vycor dishes, being essentially silica, were not found to impart any measurable quantity of a metallic element to the sample. Porcelain dishes could not be used because they were found to add copper, aluminum, and probably iron (Fig. 1). Truncated filter paper cones could not be used instead of Pyrex funnels to prevent loss by spattering, because the papers examined were found to contain measurable traces of copper and iron (Fig. 2).

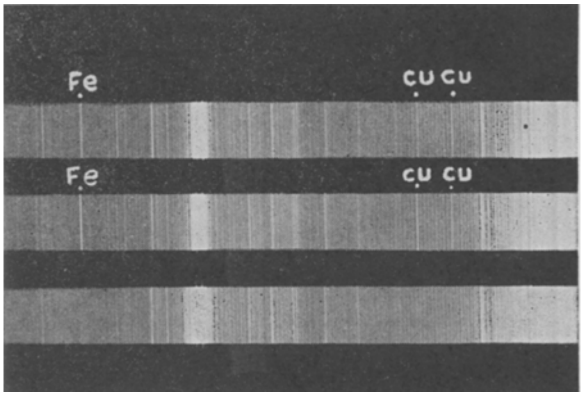

FIG. 2. Spectra of molecularly distilled oil ashed in Vycor dish with filter paper cone (upper spectrogram) and Pyrex glass funnel (lower spectrogram). Middle spectrogram is that of filter paper ash.

The initial heating of the sample and alcoholic magnesium nitrate must be slow in order to avoid flash and perhaps violent ignition of the mixture.

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*Presented at the 20th fall meeting of the American Oil Chemists' Society Oct. 30-Nov. 1, 1946 in Chicago, Ill.

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The addition of the acid solution of the internal standard must be deferred until the sample has been thoroughly charred and then evaporated without heating for the same reasons.

The magnesium nitrate performs a triple function: (1) It acts as an ashing aid. (2) The resulting oxide-carbonate mixture acts as a carrier for the extremely small amount of ash obtained from the fat or oil sample. (3) It performs the service of a spectrochemical buffer. The last function is required because the intensity of a particular atomic transition, and consequently the density of a given spectral line of a photographic plate, is dependent, somewhat, upon the matrix in which the particular element is found. Thus, for example, 1 part per million of copper in an otherwise pure sample of silica would produce a considerably more dense line than the same concentration of copper in an otherwise pure sodium chloride when arced and photographed under identical conditions.

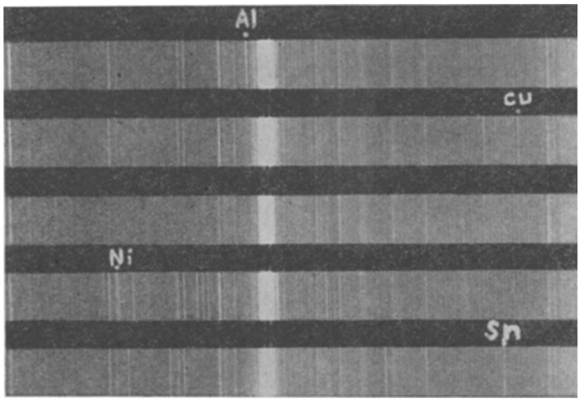

FIG. 3. Spectrograms of standards for metal analysis. Middle spectrogram is that of the molecularly distilled oil ashed with magnesium nitrate.

This method of preparing the sample reduces the spectrochemical analysis, actually, to the determination of the impurities in the magnesium oxide, contributed by the ash constituents of the original oil or fat sample. It is, also, applicable to any material that has a relatively low ash content.

The ash obtained on completion of the final ignition, at not higher than 450° C., is usually gray in color and may contain some free carbon. The low temperature lessens the possible loss by evaporation of some of the more volatile metals or their compounds. Free carbon, however, not only does not interfere with the analysis, but actually aids it. In fact, many procedures recommend the addition of small quantities of pure carbon powder in preparing the sample for spectrochemical analysis.

For the preparation of the standards required to obtain the working (or calibration) curves samples of a molecularly distilled oil are ashed as specified. Every precaution must be taken to avoid any contamination with small traces of the element to be determined. While mathematical methods have been proposed to deal with small residual traces of metals, such corrections have not been entirely satisfactory and their use further complicates the calculations. Figure 3 shows that the molecularly distilled oil and the alcoholic magnesium-nitrate solution were free of traces of metallic contaminants. Solutions of the internal standards were shown similarly to be free of the elements to be determined. At the time the internal standard solution is added to the charred sample, graded amounts of a solution of the element to be determined, varying from 0.0001% to 0.4%, as the element based on the 2.5-gm. sample, are added to a series of 2.5-gm. samples of the molecularly distilled oil. Preparation of standards by ashing individual series of molecularly distilled oil for each element is desirable in order to avoid contamination of one element by traces of impurities in another.

Preparation and Evaluation of the Spectrograms

Though the general details of the emission spectrochemical analysis are adequately given in the literature, some features of the method as applied to fats and oils warrant consideration. The spectrograph employed must have sufficient dispersion to separate the analytically important spectrum lines in the most commonly used ultraviolet region from about 2500 Å. to about 3500 Å. It has been demonstrated that the alternating current arc is not suitable (3) and that the direct current arc, operating at a relatively high current, is the most sensitive source for ash of organic materials (4). For the present work a direct current arc operating at 235 volts and 20 amperes was used. The heat generated from such a source makes water cooling of the electrode holders necessary, if high plate background, due to noncharacteristic temperature radiation, is to be avoided. For this reason hollow steel cylinder electrode holders, through which cool water may be continuously circulated, are used (Fig. 4).

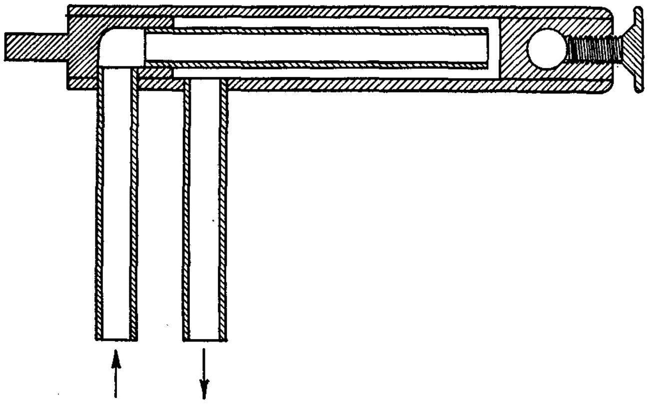

FIG. 4. Water-cooled electrode holder.

The carbon rods used must be made of the purest carbon available. Extreme care must be taken to avoid contamination of the rods during the tooling and storage of the electrodes. The positive craters, which are to become the lower electrodes and hold the sample, are shaped with a special electrode cutting tool which makes a flat-bottom cup cut to a depth of 4 mm. Figure 5 shows the spectrum of special graphite spectroscopic electrodes before and after replacement of a brass guide of the special cutting tool with a steel one. The upper electrodes may be pointed with an ordinary pencil sharpener reserved for this purpose.

In order to avoid any possibility of differences in plate densities arising from self-absorption in the arc at the high current used (5), exactly 5 mg. of the sample ash are weighed into the electrode craters for arcing. Moving plate spectrograms have shown that this size of sample of magnesium oxide will be entirely consumed in from 60 to 80 seconds. A standard exposure time of 90 seconds was adopted to assure complete burning.

By use of a rotating sector having four steps, each of the atomic lines appears on the photographic plate at four different densities, each bearing a known intensity ratio to one another. Spectrograms made in this manner are shown for typical vegetable oils in Figure 6. Most of the analytical lines for such samples do not, however, appear intense enough to be readily detected in a reproduction.

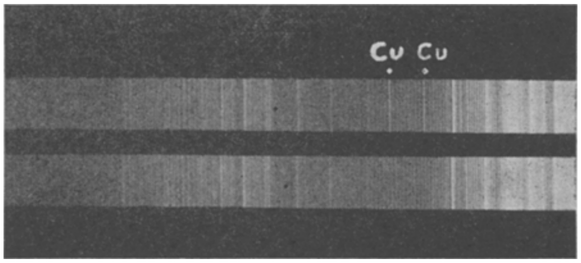

FIG. 5. Spectra of carbon rods tooled with brass guide (upper spectrogram) and with steel guide (lower spectrogram).

Eastman Spectrum Analysis No. 1 plates are satisfactory for photographing the spectral region between 2500 Å. and 3500 Å. and Eastman spectroscopic plates No. 103 A-O u.v. for photographing the region between 2100 Å. and 2500 Å. The latter are coated with a special ultraviolet sensitizing agent and have been shown to be suitable for routine analytical work (6).

Photographing of the entire four steps of the rotating sector enables all lines to be measured at suitable densities to permit either reading of all intensities from straight line portions of the plate calibration curve, or measurement of both the lines of the unknown element and of the internal standard at equal densities, as required by the D–Log E method of measurement.

In general, the spectral lines of the element being determined and of the selected internal standard should lie close to one another either to avoid differences in the slope (gamma) of the plate calibration curve if the plate calibration methods are used or to provide more or less equal background at equal densities if the D–Log E method of plate measurement is used. In addition,the lines selected for both metals should represent the same energy conditions in the arc to avoid saturation, photographic reversal, or self-absorption effects, and both metals should volatilize at about the same rate in order to assure complete burning of the entire sample. Also, all lines of both elements must be free from all interfering lines in the spectrum of the sample. Lists of suitable lines for the several elements for determination with appropriate internal standards have been published (7, 8, 9, 10, 11).

Germanium meets the requirements for a suitable internal standard for the determination of aluminum, copper, iron, nickel and manganese, and lead for the determination of tin and zinc, using the spectrum lines given in Table 1.

TABLE 1

Analytical Lines for the Spectrochemical Determination of Metals in Oils

Element	Wave length of atomic line	Internal Standard	Wave length of atomic line	Sensitivity
	Å		Å	*Parts per million*
Al	3082.16	Ge	3039.06	10
Cu	3273.96	Ge	3039.06	>0.1
Fe	3020.64	Ge	3039.06	>1
Mn	2593.73	Ge	2592.54	1
Ni	3050.82	Ge	3039.06	3
Sn	3175.02	Ge	3039.06	1
Sn	2429.50	Pb	2476.38	10
Zn	2138.56	Pb	2169.99	1

A germanium solution containing 0.1000 gm. of the dioxide (GeO_2) and 15 ml. of concentrated hydrochloric acid per liter and an aqueous solution of lead nitrate [$Pb(NO_3)_2$] containing 3.312 gm. per liter were used. One milliliter of the internal standard solution was added to each sample as specified.

The four steps of the selected lines of the elements to be determined and of the internal standards are conveniently measured with a recording densitometer.

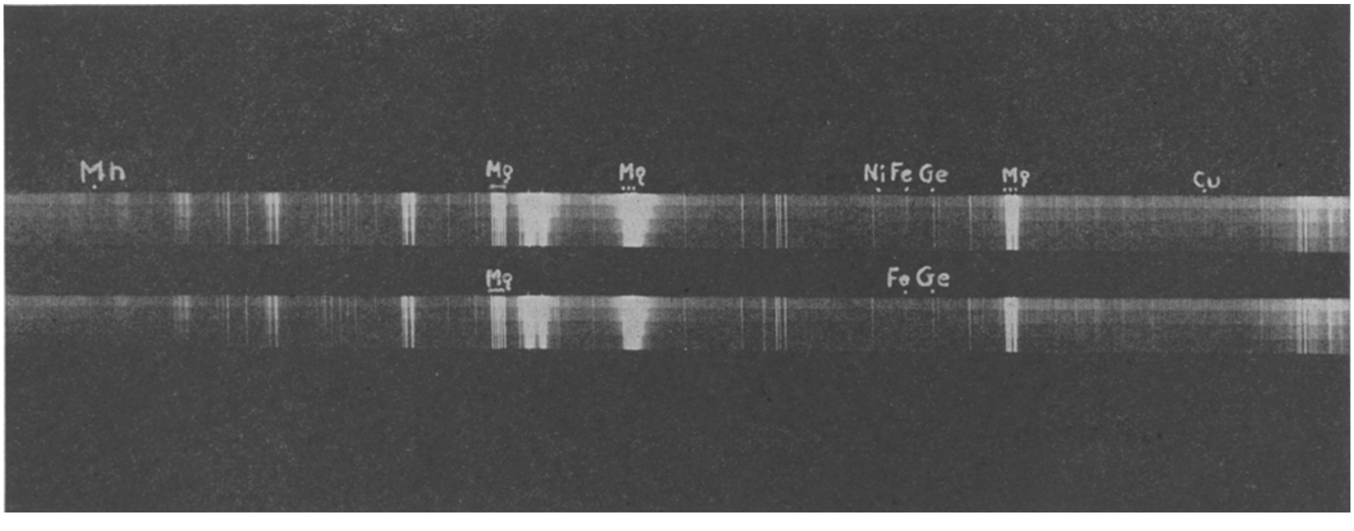

FIG. 6. Spectra of vegetable oils.

Upper spectrogram—Crude peanut oil. Lower spectrogram—Crude cottonseed oil.

This instrument gives directly the densities of the various lines. The two methods in general use for obtaining the concentration are the plate calibration (7, 12, 13) and the so-called D–Log E separation method (14, 15, 16, 17, 18, 19, 20).

The plate calibration method is illustrated by Figure 7 which shows a plate calibration curve together with the working curve used in the determination of nickel by use of the line at 3050.8 Å. and of the line of germanium (internal standard) at 3039.1 Å. To obtain the plate calibration curve (Fig. 7A) the photographic densities of the successive steps of any group of suitable lines are measured and plotted against the logarithms of the relative intensities from the known step sector factor. From this curve the measured densities of the nickel and germanium lines are converted into intensities, and to obtain the working curve for nickel (Fig. 7B) the logarithms of the ratios of these intensities are plotted against the logarithms of the known concentrations of the standards. In the analysis of oil samples the plate calibration step is repeated for each plate, and then, after obtaining the logarithm of the intensity ratio, the corresponding logarithm of the concentration is read from the prepared working curve.

The D–Log E separation method is illustrated by the measurements for the same determination in Figure 8. The densities of each of the four steps of the lines of nickel and germanium are measured, the eight values are plotted against the corresponding logarithms of the relative intensities obtained from the known step sector factor, and the separation of the two curves at a constant density of 0.3 is measured (Fig. 8A). This separation is measured for each of the standards for nickel, and plotted against the logarithms of the known concentrations to obtain the working curve (Fig. 8B). For determination of the concentrations of nickel in the samples analyzed the intensity separations are obtained in a like manner and the concentrations obtained from the working curve.

Discussion

The preparation of the oil sample for the actual spectrochemical analysis is the most time-consuming step in the method. The initial heating and drying *in vacuo* take one day and night and the final ashing in the furnace takes an additional 24 hours. The number of samples prepared at a time, however, is limited only by capacity of the equipment available.

Some preliminary tests have been made of the precision that can be expected by use of the method. For the most difficult cases, where the concentration of the metal in the oil is so low as to require densitometric measurements to be made of the minimum value that can be detected, an overall precision within ±7% can be obtained. Thus, if a particular sample is reported as containing 0.000125% nickel, repeated analyses will be expected to yield results varying from 0.000116 to 0.000134%. Tests have shown that the imprecision observed is due to the sum of very small experimental errors incurred throughout the determination from the first step in ashing through the final densitometry and calculations.

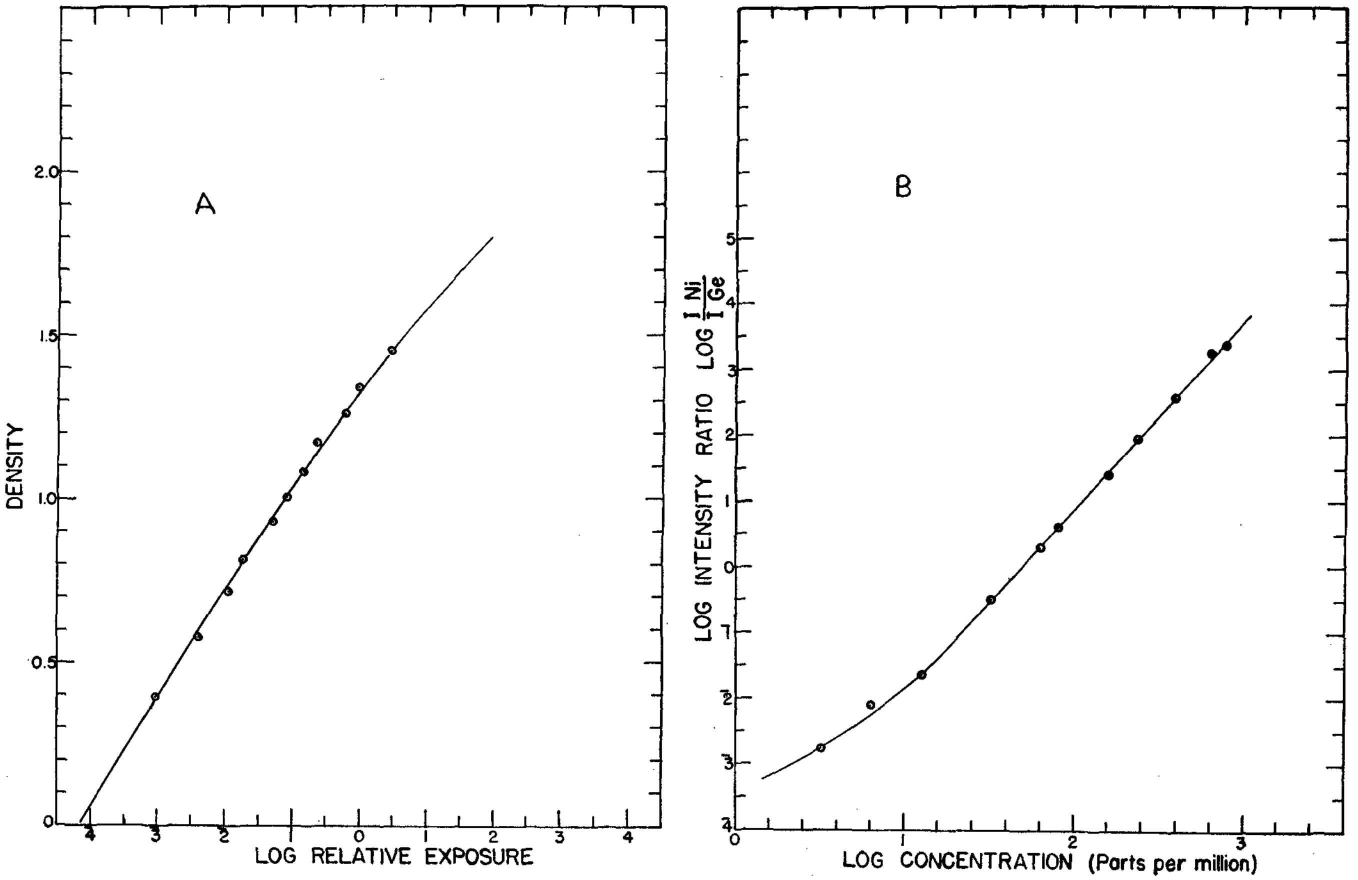

Fig. 7. Plate calibration method of plate measurement.

A. A typical plate calibration curve. B. Working curve based on intensity ratios obtained by plate calibration.

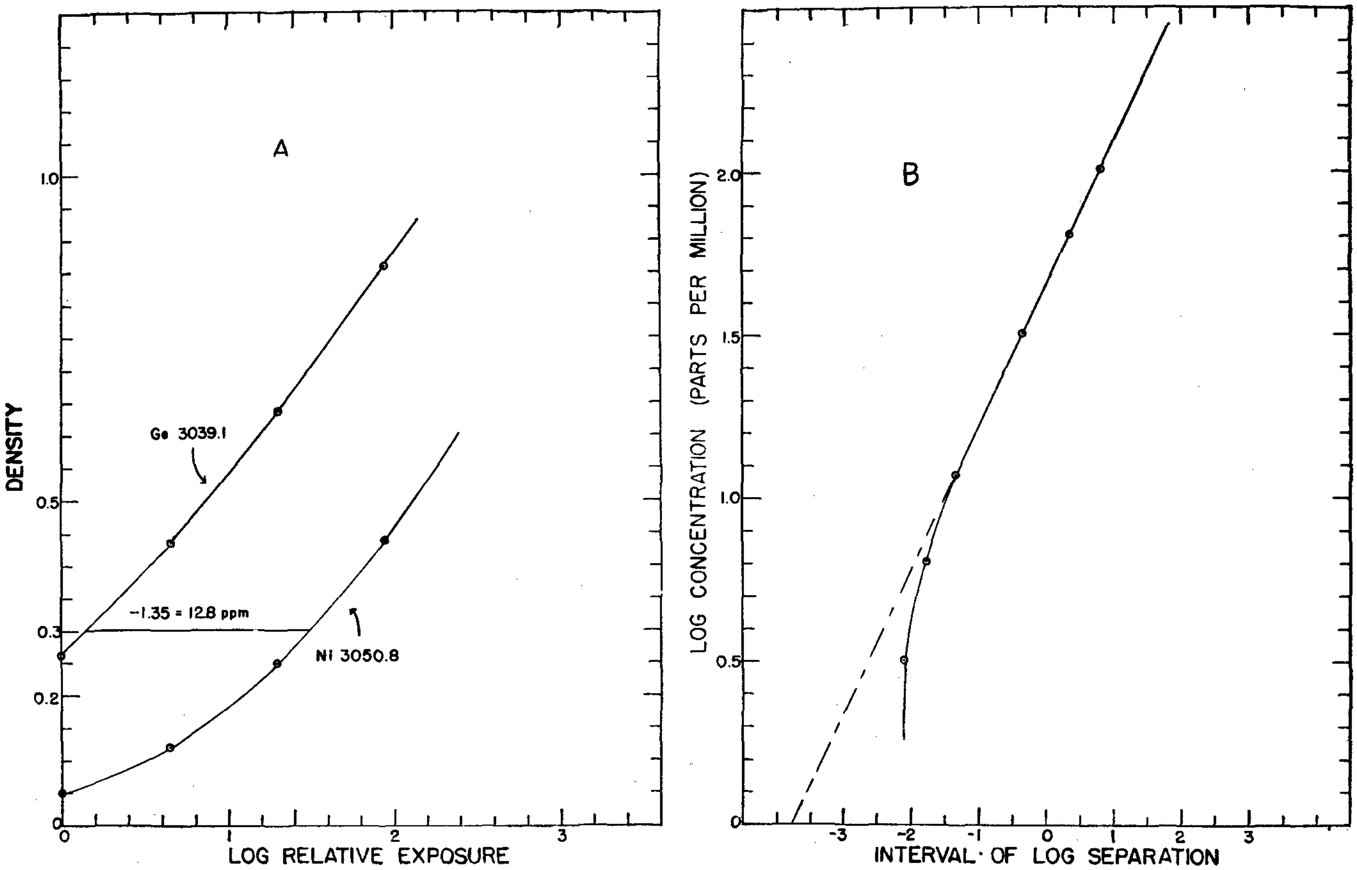

Fig. 8. The D–Log E method of plate measurement.

A. A typical interval of log separation measurement. B. Working curve based on intervals of log separation.

No tests of the accuracy of the method have been possible due to the lack of other methods of proven accuracy. However, recovery tests have indicated that the accuracy is within the variations encountered in successive determinations of a metal in the same sample of oil. The manner in which the various concentrations of the standards fall into a straight line on the working curves is in itself an indication of the accuracy of the method.

The sensitivity of the method for the determination of traces of metals in oils is of considerable importance for research purposes. Approximate limits of the sensitivity of the method for 2.5-gm. samples of oil for the determination of seven metals are given in Table 1. These data show that in general the method will permit the quantitative determination of traces of these elements when present in only a few parts per million. Increase in the size of the sample of oil ashed would enhance the sensitivity and perhaps the precision of the results.

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