Determination of Traces of Heavy Metals in Oils and Fats by Arc Spectrography

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ABSTRACT

A new and simple method is described for direct and simultaneous determination of traces in fats and oils of iron, copper, nickel, lead, silver, aluminum, magnesium, calcium and manganese. Graphite powder is used as spectroscopic buffer and for preparation of standard powders. Using necked cupped carbon electrode and cone shaped counter electrode, a steady DC arc discharge is obtained with graphite matrix. A quartz spectrograph of high resolving power is used for this determination.

INTRODUCTION

Interest in the occurrence of traces of heavy metals in oils and fats has increased in recent years. This interest derives from the association of trace metals with the origin of oils (soils and fertilizers), metal processing equipment, and catalysts used for hydrogenation; toxicity of edible oils and fats; and the effect of trace metals on the characteristics of finished products, such as color and taste.

Alkali refining and adsorption bleaching appear to remove heavy metals from oils. On the contrary, catalytic hardening seems to introduce new metallic contaminants.

Exact determination of traces of metals is a major step in evaluating and testing oils and fats, especially edible grades. It is very important to determine cumulative poisons, such as lead and probably silver; contaminants promoting rancidity, such as copper; trace metals affecting taste (copper and iron); and metals building up in kidneys (tin) (1).

With the advent of atomic absorption spectrophotometry, analysis of fats and oils for trace metals has been greatly simplified (2).

On the other hand, the spectrograph is one of the best multi-element analytical tools for determination of traces of metals. Unfortunately, not a single spectrographic assay has been recommended for the examination of oils in classical standard publications for oil and fat analysis (3-6).

Emission spectrography, this old established method of instrumental analysis, retains its main advantages: rapidity and simplicity.

Using graphite powder standards and carbon electrodes (necked cupped anode and cone shaped counter electrode), we have developed a direct method for simultaneous determination of all trace metals in oils and fats by arc spectrography. High purity graphite powder is used as spectroscopic buffer to regularize the DC arc discharge, and very pure sulfur (purified by sublimation) is added to decompose the metallo-porphyrins and bind metal traces as sulfides (7).

After addition of graphite powder and sulfur to the oil sample, the mixture is heated on a hot plate and coked finally in a muffle oven. Portions (10 mg) of the powdery residue obtained are vaporized in the cavity of carbon electrodes, and spectra are registered together with those of standard powders. Without addition of a metal ion as an internal standard, satisfactory results are obtained with a precision of ±10%.

Wet ashing of the oil or chemical enrichment of trace metals by means such as precipitation and extraction are superfluous due to the high sensitivity of detection.

EXPERIMENTAL PROCEDURES

Equipment

A Bausch and Lomb Littrow spectrograph with a fixed slit of 20 μm width and 3 mm ht is used for this determination.

National® carbon necked electrode L 3903 (Union Carbide Corp., Carbon Products Div., New York, NY) is used as anode, and National® cone shaped electrode L

TABLE I

Preparation of 500 ml Stock Solution Containing 100 μ g Metal per ml

Element	Primary substance	Quantity to be weighed (mg)	Preparation
Fe	$FeSO_4,(NH_4)_2SO_4,6H_2O$	351.15	Dissolve in water with a little dilute H_2SO_4, dilute to the mark with doubly distilled water
Cu	$CuSO_4,5H_2O$	196.5	Dissolve in doubly distilled water, dilute to the mark
Ni	$NiSO_4,6H_2O$	223.9	As above
Pb	$Pb(NO_3)_2$	79.9	As above
Ag	$AgNO_3$	78.7	As above
Al	$KAl(SO_4)_2,12H_2O$	879.5	As above
Mg	$MgSO_4,7H_2O$	506.8	As above
Ca	$CaCO_3$	124.9	Dissolve in excess dilute HCl, bring to the mark with doubly distilled water
Mn	$KMnO_4$	143.8	Dissolve in dilute HCl, reduce with excess H_2O_2, boil, cool, dilute to the mark with doubly distilled water

TABLE II

Analytical Lines and Suitable Concentration Ranges

Element	Wavelength of spectral line[a] (Å)	Range (ppm)
Fe	3020.64	1-3
Cu	3274	0.5-2
Ni	3414.76	1-3
Pb	2833.07	13
Ag	3280.68	0.5-2
Al	3082.16	1-3
Mg	2779.83	1-3
Ca	3180.52	1-3
Mn	2801.06	0.5-2

[a] See Ref. 11.

3957 as counter electrode. A 10 mg charge is weighed into the cavity.

The 3 mm distance between electrodes, or analytical gap, is further increased to 6 mm during arcing.

A 10 amp DC arc, generated from NSL Spec Power (National Spectrographic Laboratories Inc., Cleveland, OH) is used as the excitation source. The time of exposure is set to 10 sec. Pre-arcing is not necessary.

The 4 x 10 in. spectrographic plate, Kodak No. 1, is developed and dried using NSL Processor and measured with a densitometer, NSL Reader.

Reagents

High purity graphite powder, National® Spectrographic Powder L 4160, is used as buffer.

Stock solutions: For each trace metal, a stock solution containing 100 μg of metal per ml is prepared by weighing accurately a suitable primary substance, dissolving in a little doubly distilled water, and diluting to the mark in a 500 ml capacity volumetric flask. Table I lists the primary substances chosen, quantities to be weighed with an analytical balance, and methods of preparation.

Standard solutions: Stock solution (10 ml) is added to a 100 ml volumetric flask, which is brought to volume with doubly distilled water, yielding a standard solution containing 10 μg metal per ml.

Standard powders for arcing: To prepare standard powders containing simultaneously 10, 20, 30, 40, 50, and 60 ppm of each trace metal, 1, 2, 3, 4, 5, and 6 ml of each standard solution are added to six 1.000 g portions of high purity graphite powder in 6 similar 250 ml capacity Vycor beakers. After thoroughly mixing, the contents of beakers are evaporated to dryness in an oven at 105 C. The residue is scraped loose from the walls with horn spatulas and ground to a homogeneous powder in a mullite mortar.

Using graphite powder as a spectroscopic buffer, the matrix effect is practically negligible in our case.

Procedure

Usually iron, copper, nickel, lead, silver, aluminum, magnesium, calcium, and manganese are determined in every assay, the first 5 elements being considered major impurities.

Pure graphite (100 mg) and 25 mg pure sulfur are weighed into a 50 ml capacity Vycor crucible with an analytical balance. Then, 2-3 g oil or fat containing 1-6 μg of each trace metal is weighed accurately in the same crucible and mixed well. The mixture is heated on a hot plate until homogeneous, then coked in a muffle oven for 30 min at 500 C. The wt of the residue is very close to 100 mg. The graphite residue (10 mg) is vaporized in the crater of the necked electrode using 10 amp DC arc for 10 sec. Three spectra are taken from each powder. On each plate, the spectra of the 3 most suitable standard powders are registered, together with the unknowns. The suitable standards are those including the maximum and minimum concentrations that might be expected for each metal. The spectographic plate is measured according to classical procedures (8-10,12).

The analytical spectral lines and the suitable ranges, within which the density of the line is 0.1-1.0, are listed in Table II.

The lines are measured with an NSL densitometer. Corrections are made for the background of plate. Internal standard lines are not used in this method.

RESULTS AND DISCUSSION

Taking 3 spectra from each sample after conversion to graphite residue, a repeatability ca. ±10% was attained for most impurities.

To test the reliability of our method, we analyzed SP1, SP2, and SP2.5 Oil Standards, containing 1,2, and 2.5 ppm, respectively, of each trace metal and prepared by addition of special metallo-organic compounds to the blank oil. These were obtained from Cannon Instrument Company, State College, PA.

Table III shows the results obtained, expressed in ppm, together with examples of analysis of Iranian hydrogenated oils.

In arc spectrography, freedom of interference is better than in atomic absorption spectrometry because of the higher resolving power of the large spectrograph used. This is one of the factors enabling simultaneous determination of at least 9 impurities.

A large number of oil and fat samples, which we currently receive as routine work, have been tested with this method. The agreement of results with colorimetric determinations is satisfactory.

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TABLE III

Determination of Trace Metals in Oil Standards and Iranian Hydrogenated Oils Expressed in ppm

Sample	Fe	Cu	Ni	Pb	Ag	Cr	Al	Mg	Ca	Mn
SP1	1.1	0.8	0.8			1.1	0.9	1.0		
SP2	1.9	1.9	1.8			2.2	1.8	1.8		
SP2.5	2.6	2.5	2.0			2.7	2.6	2.3		
"Swan" vegetable shortening	1.0	0.7	none	0.08	0.03		0.9	1.0	1.0	0.10
"Shahpasand" vegetable shortening	0.7	0.6	none	0.09	0.04		1.0	0.7	0.25	0.07
"Jahan" vegetable shortening	0.9	0.8	0.8	0.08	none		0.8	0.7	1.0	0.10

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