Direct Determination of Traces of Heavy Metals in Canned Vegetables by Arc Spectrography

A new, simple, and rapid method for the direct and simultaneous determination of traces of iron, copper, lead, tin, silver, and manganese in brined canned vegetables is described. Pure graphite powder is used as spectroscopic buffer and for the preparation of standard powders. Pure sulfur is added to the sample before calcination to bind trace metals as sulfides and prevent volatilization. A quartz spectrograph of high resolving power is used for this determination.

The determination of traces of heavy metals in canned food has assumed considerable importance in recent years. This derives from the association of trace metals with the corrosion of processing equipment or of metal containers, especially when strong electrolytes (vegetables in brine) or acidic liquids (fruit juices) are concerned, with the consequences to food of toxicity or bad taste.

The exact determination of traces of metals is a major test in quality control of canned food and in the evaluation of taste and color. It is very important to analyze for cumulative poisons such as lead and mercury and for contaminants which cause color change (Grove, 1971) or unacceptable taste (iron and copper) in the food.

The spectrograph is one of the best multielement tools for the determination of traces of metals. Emission spectrography, this long-established method of instrumental analysis, still retains its main advantages: rapidity and simplicity.

Using high-purity graphite powder as spectroscopic buffer and as a regulator of direct current (DC) arc discharge and extrapure carbon electrodes, we have developed a direct method for the simultaneous determination of traces of Fe, Cu, Pb, Sn, Ag, and Mn in canned vegetables. Chemical enrichment of traces by precipitation, extraction, or ion-exchange is superfluous due to high detection sensitivities.

As the concentration of trace metals is usually larger in the brine than in the vegetables, this determination reduces to an analysis of the brine, which is normally a dilute solution of NaCl containing 5–25 g of salt/L.

Very pure sulfur (obtained by double distillation) is added to the brine under analysis before coking to prevent loss of volatile trace metals (Agazzi et al., 1963).

EXPERIMENTAL SECTION

Equipment. A Bausch & Lomb Littrow spectrograph with a fixed slit, 20 μm wide and 3 mm high, is used for this determination.

A National carbon necked electrode L 3903 (Union Carbide Corp., Carbon Products Division, New York) is used as the anode. This anode is similar to S-13 (ASTM Designation: E 130 – 63 T). The thin-walled cup allows a complete burn-off. The undercut pin allows greater heating of the sample. A 10-mg charge is weighed into the cup.

A National cone-shaped electrode L 3957 is used as counter electrode. This is similar to C-5 (ASTM designation: E 130 – 63 T) and allows greater arc stability.

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

A 10 A DC arc, generated from NSL Spec Power (National Spectrographic Laboratories Inc., Cleveland, OH), is used as the excitation source. Exposure time is set at 10 s. Pre-arcing is not necessary.

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

Procedure. Pure graphite (100 mg) and 25 mg of pure sulfur (to bind metal traces as sulfides) are weighed into a 50-mL capacity Vycor crucible with an analytical balance; then, 10–15 g of brine containing 0.2–1.2 μg of each trace metal and 0.1–0.15 g of NaCl are weighed accurately into the same crucible and mixed well. The mixture is heated to dryness on a hot plate and then coked in a muffle oven for 30 min at 600 °C. The weight of the residue is determined accurately and the evaporation ratio is calculated. The graphite residue (10 mg) is vaporized in the crater of the necked electrode using a 10 A DC arc for 10 s. Three spectra are taken from each powder. On each plate, the spectra of the three most suitable standard powders are registered together with those of the unknowns. Suitable standards are those including the maximum and minimum concentrations that might be expected for each metal. The spectrographic plate is measured according to classical procedures (ASTM, 1964).

The analytical spectral lines and the suitable ranges, within which the density of the line is 0.1 to 1.0, are listed in a previous paper (Farhan and Pazandeh, 1976). The analytical line chosen for tin is Sn 2840.0 Å.

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

Stock solutions and standard solutions (10 μg of metal/mL) are prepared as outlined in a previous paper (Farhan and Pazandeh, 1976).

To prepare a stock solution for tin, dissolve 0.1000 g of pure metal in 10 mL of concentrated HCl and dilute to 1 L with doubly distilled water. A standard solution is made by diluting ten times in a 100-mL volumetric flask.

Synthetic Standard Powders for Arcing. When the brine is coked, the residue is usually an impure sodium chloride containing some unburnt graphite which is added before calcination. Synthetic standard powders are made by adding known amounts of trace metals to a mixture of sodium chloride, graphite, and sulfur powders and coking at 600 °C.

To prepare standard powders containing 1, 2, 3, 4, or 5 ppm of each trace metal simultaneously, 2, 4, 6, 8, or 10 mL of each standard solution (10 μg of metal/mL) are added to five 1.000-g portions of NaCl, in five similar 250-mL capacity Vycor beakers, each containing 1.000 g of high-purity graphite powder and 0.250 g of pure sulfur.

After thorough mixing, the contents of the beakers are evaporated to dryness in an oven at 105 °C and then coked in a muffle oven for 30 min at 600 °C. The weight of the residue is determined accurately after cooling. This is usually different from the weight of the initial NaCl taken (1.000 g). Exact ppm values are calculated for the final weight after calcination. The residue is scraped loose from the walls of the beaker with a horn spatula and ground to a fine powder in a mullite mortar.

RESULTS AND PRECISION

To illustrate the repeatability of our method, ten 10-g brine samples were taken from the same can (Vita brand peas, Tehran) and trace metals were determined as usual.

Table I. Trace Analysis of Ten Samples Taken from the Same Can (Vita Brand Peas) Expressed in ppm

sample no.	Fe	Cu	Pb	Sn	Mn
1	1.40	0.12	0.29	0.06	0.25
2	1.28	0.13	0.31	0.03	0.21
3	1.37	0.12	0.32	0.07	0.25
4	1.13	0.13	0.31	0.05	0.20
5	1.43	0.11	0.26	0.06	0.20
6	1.18	0.15	0.33	0.03	0.24
7	1.85	0.14	0.28	0.03	0.24
8	1.64	0.15	0.34	0.04	0.20
9	1.32	0.11	0.29	0.03	0.18
10	1.12	0.15	0.34	0.05	0.27
$\bar{x}$	1.372	0.131	0.307	0.045	0.224
SD	0.2296	0.0159	0.0267	0.0151	0.0295
coeff. of variation, $(s/\bar{x}) \times 100$	16.7	12.2	8.7	33.5	13.2

Table II. Determination of Trace Metals in Iranian Canned Vegetables Expressed in ppm

sample	brine concn, g of NaCl/ L	Fe	Cu	Pb	Sn	Ag	Mn
vine leaves (shemshad)	25.4	6.0	0.03	0.05	0.02	0.08	0.10
peas (Tehran)	25.4	2.8	0.20	0.45	1.00	0.03	0.01
green beans (vita)	4.5	2.1	0.08	0.01	0.30	0.08	0.25

The results obtained are given in Table I. The average, $\bar{x}$, standard deviation, $SD = \sqrt{\sum d^2/(n-1)}$ (where d = difference between individual result x_i and the average, and n = number of results), and coefficient of variation, $(100/\bar{x}) \times s$, are calculated for each trace metal.

The coefficient of variation may be taken as a measure of repeatability precision. This precision is, as usual, a function of concentration and is 100% for detection limit. It also depends on the particular metal determined.

It can be seen from Table I that the precision of this method is within 9-17% for most trace metals and much lower for tin (0.05 ppm).

As far as accuracy is concerned, we believe that it is close to the above-mentoned precision. Since the standard powders are synthetic and are treated in exactly the same way as the samples analyzed, the method seems to be self-sufficient and independent (Harvey, 1950). It is also equivalent, by its nature, to a recovery test, and matrix effect is either minimized or canceled out.

A large number of Iranian cans of vegetables have been tested with this method. Detailed results may be obtained on request. Table II shows examples of typical results.

While the results for Fe exceed allowable limits (tolerance is 0.1 ppm), Cu, Mn, and Sn are within the limits (0.1-0.2 ppm). Fortunately, the amounts of cumulative poison Pb do not exceed 2 ppm, the usual tolerance (Grove, 1971).

LITERATURE CITED

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