Metal Analysis of Edible Fats and Oils by Atomic Absorption Spectrophotometry[1]

ULF PERSMARK and BENGT TOREGARD,
Research Laboratory, AB Karlshamns Oljefabriker, Karlshamn, Sweden

Abstract

Enrichment procedures for trace metal analysis by atomic absorption spectrophotometry have been investigated. The detection limits are primarily determined by the enrichment factor and the accuracies have been found to be roughly the same within the same absorption ranges independent of the method used.

Introduction

The presence of small amounts of metals in edible oils and fats is well known to have serious deteriorating effects on quality. Since small amounts in this field include quantities far below 1 μg/g, there will consequently arise analytical difficulties, when these amounts are to be determined with acceptable reproducibility.

The classical analytical methods for metal determinations have been reviewed by Snell and Snell (1). For organic materials these methods are generally preceded by heat destruction procedures, e.g., ashings, before the metals are available for quantification. Besides they are not always suitable for the determination of trace metal contents, which is most often of interest in the oil and fat field. The concentrating procedures, which must be performed in order to acquire measurable quantities, often seriously influence the accuracy. They are also very time consuming.

Colorimetric methods, which allow direct determinations of metals in glyceride oils and fats, have been reviewed by Newlove (2). Even if they are specially adjusted to suit trace contents of metals in oils and fats, they are obviously not sufficient when "traces" means less than one μg/gm.

The advantages of atomic absorption spectrophotometry (AAS) are primarily its relatively high sensitivity, which to a certain extent eliminates enriching procedures, and its specificity, which minimizes errors due to other metals present in the sample. Such contaminations are often an outstanding problem when classical colorimetric methods are to be used.

Without considering accuracy for the moment, the lowest detection levels are approximately around 0.1 μg/gm when using AAS without any specific prepreparation (3). Considerable variations exist, however, depending on the actual analytical conditions, such as instrumentation, type of element, and special arrangements aimed for example at increasing sample flow to the burner (4).

Essential factors which should be emphasized when discussing sensitivity and detection ranges are the accuracy and reproducibility. These factors must be considered in order to give meaning to detection levels. Determinations of metals by AAS directly on the oil or fat require dilution of the samples by an appropriate solvent when using the conventional burner types. Otherwise irregular sample flows arise from the viscosity of the oil. The higher the concentration of metals in the flame, i.e., the more concentrated the solution, the higher the sensitivity should be. Because of the very low metal contents the most concentrated solutions possible must be used. The dilution factor, normally around 1:10, decreases sensitivity (3).

Direct analyses of metals in oil and fats by AAS has several practical advantages: It is fast, simple and thus very suitable for routine work. Since it includes a minimum of preparation procedures, the error potential of the analysis should theoretically also have been lowered to a minimum. However the difficulties which do exist in the direct analysis made us consider other alternatives. We decided to investigate a few common enrichment and cleaning up methods, i.e., elimination of the fatty material, in part to clarify the detection limit and accuracy compared to direct analysis, and in part to see if any of these preparations would allow us to measure quantities of metals lower than permitted by direct analysis. The methods which were investigated are described below (1–5).

Experimental Procedures

Methods

All chemicals and solvents were of reagent grade. (1) A sample of 2.5 g oil with 2.5 g of dichloroacetic acid was diluted to about 20 ml with methylisobutyl ketone (MIBK) and heated to 50 C for 5 min. The solution was cooled to room temperature, made up to exactly 25 ml with MIBK and directly analyzed. The instrumental parameters used are shown in Table I. Operators should recognize that any chlorine-containing organic compound might give off toxic fumes, and take necessary precautions. (2) A 10 g sample of oil-fat was weighed in a quartz crucible. The fatty matter was eliminated according to the following steps: (a) smoking off on a hot plate at 100–150 C for 1 hr; (b) ashing in an oven at 400–450 C for 2 hr; (c) continued ashing at 500–550 C over night. The ash was then wet with nitric acid at 500–550 C for 1–2 hr more until the organic material was completely destroyed. The crucible was washed with 1 ml of hot nitric acid, twice with 1 ml of dilute nitric acid, and twice with 2.5 ml of distilled water. The washings were then made to exactly 10 ml with distilled water and immediately analyzed (Table I). Ashing of oils to retain metals

TABLE I
Instrumental Parameters

Method	Sample flow, ml/min	Noise suppression setting	Scale expansion	Slit[a]	Gas mixture pressure-flow[b]	
					Acetylene	Air
1[c]	6	2	×10	2	8:8	25:12
2	8	2	×3	3	8:9	30:9
3	8	2	×3	3	8:9	30:9
4	8	2	×3	3	8:9	30:9
5	8	2	×3	3	9:6	25:12

[a] Slit 2 equivalent to slit opening of 0.1 mm; slit 3 equivalent to slit opening of 0.3 mm.
[b] Readings on Perkin-Elmer model 220 Burner regulator.
[c] Preheated air and atomizer.

[1] One of 28 papers presented at the Symposium, "Metal-Catalyzed Lipid Oxidation," ISF-AOCS World Congress, Chicago, September 1970.

TABLE II

Absorption Measurements of Nickel in Oil Standards, Absorption Readings ($\bar{X}$)[a] and Relative Standard Deviations (S).[b]

Ni, μg/gm	5		2		1		.5		.2		.1		.05		.02		.01		.005		Noise, % A
Method	$\bar{X}$, %	S %																			
1	7.22	4.55	2.83	18.0	1.54	25.3	0.82	35.4	0.38	60.4	0.15	79.4									0.37
2	17.11	2.82	7.84	17.4	3.69	22.4	2.25	14.8	1.37	38.9	0.70	36.3									0.37
3	16.61	7.59	7.29	11.8	3.66	15.3	1.85	15.8	1.00	10.7	0.51	14.9									0.33
4									6.89	7.8	3.53	5.4	1.78	11.3	0.77	20.8	0.46	28.1	0.42	59.3	0.46
5									20.03	27.4	8.63	20.8	4.79	18.4	1.53	40.5	0.78	79.5	0.92	18.3	0.31

[a] Mean values ($\bar{X}$) for $n = 7$.

[b] $S = \frac{3}{\bar{X}} \times 100$ (%).

TABLE III

Simulated Determination of "Unknown" Sample Using a Standard Curve

Method	"Unknown" sample, μg/gm Ni: Theoretical	"Unknown" sample, μg/gm Ni: Found[a]	Standards, μg/gm Ni	Relative standard deviation[b]	Interval ± of 95% confidence[c]
1	2.0	1.91	5.0 and 1.0	5.1	0.17
	0.2	0.22	0.5 and 0.1	17.9	0.07
2	2.0	2.39	5.0 and 1.0	43.4	1.72
	0.2	0.27	0.5 and 0.1	29.3	0.13
3	2.0	2.09	5.0 and 1.0	13.3	0.47
	0.2	0.25	0.5 and 0.1	19.8	0.08
4	0.1	0.10	0.2 and 0.05	3.8	0.006
	0.02	0.020	0.05 and 0.01	18.5	0.006
5	0.1	0.094	0.2 and 0.05	13.8	0.022
	0.01	0.010	0.02 and 0.005	85.0	0.014

[a] Mean value of seven determinations.

[b] $\frac{3}{\bar{X}} \times 100$ (%).

[c] Duplicates.

may need further study. (3) A 20 g sample was diluted with 50 ml of isooctane and then extracted with 20 ml of hydrochloric acid: water (1:3) with stirring and refluxing for 40 min. After cooling, the water phase was drawn off and analyzed (Table I). (4) As in Method 3 but 100 g of fat-oil extracted with 10 ml of hydrochloric acid: water (1:3) containing .03% EDTA (5). (5) A sample of 40 g of fat in 50 ml of isooctane was extracted with hydrochloric acid as in Method 3. The water phase was then transferred to a 50 ml graduated bottle. The acidic solution was neutralized with 25% ammoniac solution, about 5 ml, to yellow colour (indicator: m-cresolsulfone-phthalein, pH range: 7.4–9.0). Ammonium pyrrolidine-dithiocarbamate solution (2% in water: 1 ml) was added. The solution was extracted with 5 ml MIBK for 5 min. The organic phase was drawn off and analyzed (Table I).

Preparation of Standards

Nickel in oil standards were prepared from a "metal-free" rapeseed oil (double bleached, citric acid treated and deodorized) stock solution containing 500 μg/gm nickel (as Ni-cyclohexanebutyrate). "Metal-free" oil: the same rapeseed oil was used as a zero-line reference during the measurements. (All standards were kept in polyethylene bottles.)

Instrumentation and Calculations

The measurements were performed on a Perkin-Elmer model 303 double beam atomic absorption spectrophotometer fitted with high intensity hollow cathod lamps. The emission line at 2320 Å was used. Combustion gas-acetylene/air mixture.

Seven independent measurements were made on each standard sample. Mean values and standard deviations were calculated for each concentration. Furthermore some "real" analyses were simulated by measuring two standards for constructing a standard curve and then determining the nickel content of an "unknown" sample with a metal content lying between those of the references used.

Results and Discussion

Table II shows the results of the absorption measurements of the standard nickel in oil samples with the various preparation methods. It quite clearly demonstrates that for higher levels of metal contents, i.e., 5–1 μg/gm, there is no substantial difference between Methods 1, 2 and 3, although there is a slight trend that the reproducibility seems to decrease more rapidly for Method 1 and less for Method 3, when concentrations move nearer to 1 μg/gm. Moving further down in metal concentrations to 0.1 μg/gm, this trend is quite obvious. The practical consequences are that under present experimental conditions direct determination of metals equivalent to nickel in oils should be quite satisfactory down to the range of one μg/mg corresponding to an absorp-

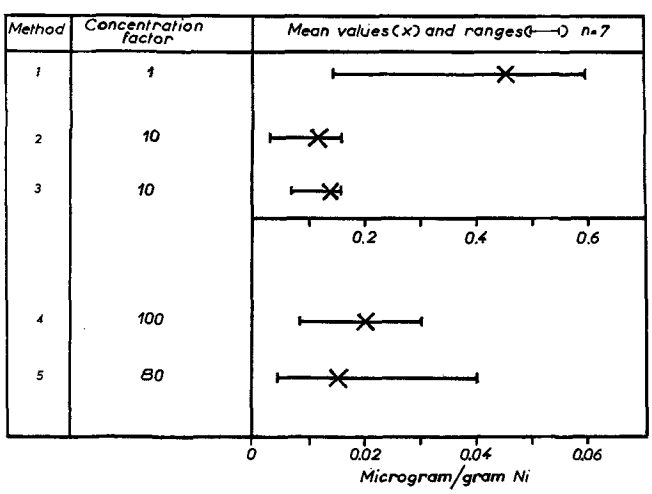

FIG. 1. Detection limits (2 × noise level): mean values and ranges, $n = 7$.

tion reading of about 1–2%. Only Methods 4 and 5 permit measurements of quantities below 0.1 μg/gm. This result depends primarily on the higher metal concentration in the final solution. Detection limit ratios and final concentration ratios are roughly reversibly proportional (Fig. 1). Lower reproducibility of Method 4 compared to 5 is caused by considerably higher blank values of the former. Furthermore it may be generally stated as a simple rule that the absorption reading must reach 1–2% in order to be able to quantify the metal content. The so-called noise levels are also fairly constant.

The results from the simulated determinations (Table III) should generally demonstrate lower accuracies than those in Table II. This effect occurs because two measurements have been performed, i.e., on the sample and on the references, and the errors from the measurements on references will be involved in the following determination of the sample.

REFERENCES

1. Snell, F.D., and C.T. Snell, in "Colorimetric Methods of Analyses," D. Van Nostrand Co., Inc., New York, 1949.
2. Newlove, T.H., in "Laboratory Handbook for Oil and Fat Analysts," Edited by L.V. Cock and C. von Rede, Academic Press, London, 1966.
3. Persmark, U., Proceedings: "Metal Catalyzed Lipid Oxidation," Edited by R. Marcuse, SIK Publication No. 240, Gothenburg, Sweden, 1968, p. 43.
4. Bladh, E., Ibid., p. 49.
5. Deck, R.E., and Kaiser, K.K., JAOCS 47: 126 (1970).

[Received May 27, 1971]