Determination of Traces of Cadmium in Biological Materials by Atomic Absorption Spectrophotometry

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A quantitative determination of cadmium in some foods of plant and animal origin by atomic absorption spectrophotometry is described. The content of cadmium in foods may be determined by atomic absorption by direct measurement of the mineralized product.

Quick and reliable determination of trace elements, namely of heavy metals, in biologic materials is recently gaining importance in a number of biological and technical areas. Although a number of existing analytical methods are of satisfactory accuracy and sensitivity, the analytical procedure itself requires extensive manipulation with the material being tested.

Atomic absorption spectrophotometry fulfills most of the demands for quantitative determination of trace cations in various environments. It is comparatively simple, quick, sufficiently sensitive, and reliable, usually not requiring complicated preliminary processing of the sample. This method was first described by Walsh (1955).

In foods of animal and plant origin, cadmium was studied also rarely (Schroeder and Balassa, 1963; Schroeder *et al.*, 1967). In our report we describe the method of determination of cadmium traces in some foods by atomic absorption spectrophotometry.

EXPERIMENTAL

All glass vessels and pipets were washed before use in the manner usual in trace analysis. For preparation of solutions, deionized water was used. All reagents applied were ultrapure. Ammonium hydroxide and hydrochloric acid were distilled into deionized water isothermally.

Apparatus. The atomic absorption spectrophotometer Techtron, type AA-4, was used in this work.

Technical Conditions. High intensity lamp ASL Ltd., wavelength 2288 nm, lamp current 3 mA, slit-width 200 μm and photomultiplier type R-213, was used. Two kinds of heating mixture were used: for air/acetylene mixture we used the burner AB 41 (slot 10 cm $\times$ 0.5 mm) with acetylene flow gage reading 3.5 and pressure 10 psi; for air/propane mixture we used the burner AB 42 (slot 10 cm $\times$ 1.5 mm) with flow gage reading 2.5 and pressure 10 psi. Air pressure was 15 psi in both cases.

Preparation of Standards. Pure metal cadmium (0.1 g) was dissolved in a small volume of hydrochloric acid and diluted with water to a 1000-ml volume. From this supply solution fresh standard solutions were prepared before each measurement to the amount of 0.00–0.08 ppm Cd, 0.1–0.8 ppm Cd, and 1.0–6.0 ppm Cd.

Preparation of Samples. Samples of foods were mineralized by a mixture of sulfuric, perchloric, and nitric acid. After partial neutralization at pH 5–6 the cadmium content was determined by means of atomic absorption spectrophotometry.

Parallel food samples were, after mineralization, neutralized by ammonium hydroxide, 0.2 *M* acetate buffer of pH 10.7 was added, and pH treated by ammonium hydroxide to 10.7 (*cf.* Bibr *et al.*, 1969). Cadmium was extracted by 5×10^{-4} *M* dithizone solution in chloroform. After adding $HClO_4$, the organic dithizone phase was evaporated and the evaporation residue dissolved in 0.01 *N* HCl. Then the cadmium concentration in the solution obtained was determined by atomic absorption.

RESULTS

The calibration curves, when heating mixtures air/acetylene and air/propane were used, showed a straight-line course in the range from 0.0 to 1.0 ppm Cd, but the sensitivity of determination in air/propane flame was higher. We used, therefore, the heating system air/propane for the determination of cadmium content in foodstuffs. Calibration curves for indirect determination of cadmium were obtained by extraction of standard solutions containing varying amounts of cadmium with 5×10^{-4} *M* solution of dithizone in chloroform.

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Table I. Reproducibility of Method

Sample, ppm Cd	Number of measurements	Extent	M[a]	S.E.[b]	Coefficient of variation, %
0.02	20	0.013–0.027	0.021	0.0022	10.5
0.04	20	0.035–0.048	0.043	0.0044	10.2
0.06	20	0.056–0.063	0.060	0.0023	3.8
0.40	20	0.420–0.440	0.430	0.0220	5.1
1.00	20	0.930–1.180	1.050	0.0810	7.7
3.00	20	2.860–3.210	3.040	0.0790	2.6
5.00	20	4.810–5.260	5.160	0.0930	1.8

[a] M = mean. [b] S.E. = standard error.

Reproducibility. Reproducibility of method was determined by repeatedly measuring the absorbance of solutions containing 0.02, 0.04, 0.06, 0.4, 1.0, and 5.0 ppm of cadmium (Table I).

Interference. We followed up the disturbing effect of some cations and anions by modifying the procedure used by Chakrabarti (1968). Interference was determined by adding 100 ppm of the respective ion to standard solution containing 1 ppm of cadmium (Tables II and III).

DISCUSSION

Sensitivity of cadmium determination by atomic absorption spectrophotometer Techtron AA-4 is stated by the producer

Table II. Anionic and Cationic Interferences

	Absorbance					Absorbance			
Anion[a]	Air/acetylene	Interference	Air/propane	Interference	Cation[a]	Air/acetylene	Interference	Air/propane	Interference
Cd^{2+}	0.135	–	0.237	–	Cd^{2+}	0.135	–	0.237	–
SO_3^{2-}	0.130	–	0.231	–	Cu^{2+}	0.132	–	0.235	–
CO_3^{2-}	0.134	–	0.238	+	Mg^{2+}	0.135	None	0.237	None
HCO_3^-	0.133	–	0.234	–	Zn^{2+}	0.140	+	0.225	–
SiO_3^{2-}	0.138	+	0.239	+	Hg^{2+}	0.130	–	0.235	–
					Ca^{2+}	0.132	–	0.239	+
					Ba^{2+}	0.137	+	0.242	+
					Na^+	0.146	+	0.233	–
					Fe^{3+}	0.136	+	0.239	+
					Co^{2+}	0.138	+	0.240	+
					Ni^{2+}	0.138	+	0.236	–

[a] The disturbing anions were in the form of sodium and potassium salts; the cations were in the form of chlorides or nitrates.

Table III. Recovery Test

Sample	No. of sample	Wet weight of sample, g	Cd added, ppm	Cd recovered, ppm	Recovery, %	Sample	No. of sample	Wet weight of sample, g	Cd added, ppm	Cd recovered, ppm	Recovery, %
Milk	1	10.0		0.10	100	Potatoes	1	2.0		0.18	100
	2	10.0	0.4	0.49	98		2	2.5	0.4	0.68	117
	3	10.0	0.4	0.52	104		3	2.5	0.4	0.65	112
	4	10.0	1.0	1.15	105		4	2.0	1.0	1.20	102
	5	10.0	1.0	1.08	98		5	2.4	1.0	1.41	119
	6	10.0	1.0	1.09	99		6	2.0	1.0	1.19	101

Table IV. Cadium Content in Some Foods

(μg/g wet weight)

Sample	No. of analyses	Direct measurement		Measurement after extraction		P,[c] >
		M[a]	S.E.[b]	M	S.E.	
Celery	5	0.058	0.013	0.059	0.011	0.01
Parsley	4	0.088	0.077	0.086	0.006	...
Garlic	5	0.077	0.001	0.075	0.001	...
Carrot	5	0.086	0.024	0.089	0.016	...
Onion	5	0.047	0.003	0.046	0.002	...
Potatoes	5	0.092	0.002	0.090	0.002	...
Milk	5	0.010	0.003	0.012	0.003	...
Egg yolk	4	0.120	0.005	0.121	0.004	...
Egg white	4	0.076	0.004	0.073	0.005	...

[a] M = mean. [b] S.E. = standard error. [c] P = significance of difference between direct measurement and measurement after extraction.

to be of value 0.02 ppm at 1% absorption, *i.e.*, at 0.0044 absorbance. We achieved this sensitivity using heating system air/propane. At application of air/acetylene system, sensitivity 0.06 ppm was achieved. In this case lower sensitivity is caused probably by the fact that in application of acetylene heating mixture, we did not purify acetylene before combustion. When measuring standards and also samples of very low cadmium content, when value of transmittance moved within limits of 90–99%, we applied scale expansion 5×.

It is obvious from the value of coefficient of variation (Table I) that the method is reproducible if cadmium is determined in concentrations from 0.06 ppm upwards.

When extracting cadmium from sample by dithizon, we applied our own modification of procedure, suggested by Kubota *et al.* (1968). There is nevertheless, as is evident from Table IV, no statistically significant difference between both methods applied by us for measurement of cadmium in sample, *i.e.*, between direct measurement in the mineralizate and measurement after extracting cadmium in the sample by dithizon (statistical evaluation was carried out by Student's t test).

No interferences of perchloric, hydrochloric, sulfuric, and nitric acid on cadmium determination was observed.

When studying the effect of interference ions upon cadmium determination in samples, we found that in content of 1 ppm Cd in aqueous solution, the effect of the ions does not manifest or manifests at quite a minimum.

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