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Food Chemistry 67 (1999) 311–316

Food Chemistry

www.elsevier.com/locate/foodchem

Analytical, Nutritional and Clinical Method section

A quartz crystal microbalance method for the determination of iodine in foodstuffs

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Received 4 December 1998; received in revised form and accepted 1 April 1999

Abstract

A quartz crystal microbalance (QCM) method to estimate the iodine content in foodstuffs is proposed. The method is based on sensitive response to mass change at electrodes of piezoelectric quartz crystal. After samples are decomposed, ionic iodine in the sample solution is changed to free iodine in acidic environment. Free iodine is then adsorbed at gold electrodes of QCM and iodine content in samples is estimated through decrease of QCM frequency. The method showed good reproducibility. Recovery of different concentrations of iodine added to food ranged from 93.2%-101.1%, with a mean and standard deviation of 96.9 ± 3.2 %. The detection limit of the method for iodine is 0.0005 mg/l in aqueous solution. No significant interferences are caused by anions such as Cl^-, F^-, NO_3^-, SO_4^{2-}, PO_4^{3-} and cations such as K^+, Na^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Bi^{3+}. The only interference is found from bromine. The assay is also applicable for the determination of iodine in biological samples such as serum and urine.

Keywords: Quartz crystal microbalance; Iodine; Food

1. Introduction

Iodine is an essential nutrient for normal thyroid function. The US recommended dietary allowance for iodine has been set at 150 μg daily for adults (National Research Council, 1980). Chronic low or high iodine intake affects thyroid function. In particular thyroid disorders due to excessive iodine intake have become of interest in recent years (Talbot, Fisher & Carr, 1976). Therefore, an assessment of iodine intake is important and an available, sensitive method to determine iodine in foods is required. For this purpose, the colorimetric methods (Fisher, L'Abbe & Giroux, 1986; Lauber, 1975) based on the Ce–As–I catalytic reaction are used widely.

Methods using ion-selective electrode (Dellavalle, 1984), gas-liquid chromatography (Baker, 1977; Mitsuhashi & Kaneda, 1990), differential pulse polarography (Curtis & Hamming, 1982; Thompson, Lee & Allen, 1983) and Auto-Analyzer (Moxon & Dixon, 1980) have been reported for the determination of iodine content of foods. However, most of these methods demand sophisticated laboratory equipment.

Recently the quartz crystal microbalance (QCM) has been used as mass sensor in vacuum and gas phase experiments (Alder & McCallum, 1983; Guilbault, 1982). The low cost and conceptual simplicity of this method portend its development in a diverse variety of commercial and research applications. The response of the QCM is extremely sensitive to mass changes at the electrodes of the crystal. It provides information that would be difficult to obtain with other methods.

This paper reports on a relatively simple QCM method for the determination of iodine in foods. Generally, iodine exists in sample solutions in the form of ionic iodine after the samples are decomposed. The ionic iodine is changed to free iodine in acidic environment. Free iodine is then extracted into the carbon tetrachloride phase and adsorbed at gold electrodes of QCM from the carbon tetrachloride solution. The iodine content in sample is estimated through decrease of QCM frequency. By the proposed method, iodine content in food such as milk and apple, etc., and body fluids such as urine and blood, etc., was determined successfully.

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0308-8146/99/$ - see front matter
PII: S0308-8146(99)00121-1

2. Principle

The quartz crystal microbalance (QCM) is designed around a piezoelectric wafer sliced from a single crystal of quartz. As a piezoelectric material, the quartz wafer deforms slightly in the presence of an electric field. When used in the QCM, the quartz wafer is sandwiched between two electrodes bonded to the wafer surface. These electrodes are used to induce an oscillating electric field perpendicular to the surface of the wafer. This oscillating electric field produces a mechanical oscillation, a standing wave, in the bulk of the quartz wafer.

The frequency of this coupled mechanical and electrical oscillation in the QCM depends on several factors. Factors that are normally constant include the physical properties of the quartz wafer (thickness, density, and shear modules). Factors that sometimes are held constant include the density and viscosity of the phases adjacent to either side of the QCM wafer (gas or liquid), pressure differences across the wafer, and the temperature. Factors that often change are the mass of the attached electrode or the mass of an adsorbate or thin film attached to that electrode. These variations in mass are usually probed with the QCM.

For many cases, interfacial mass changes are related in a simple manner to change in the QCM oscillation frequency, through the Sauerbrey (1959) equation,

$$\Delta f = -2\Delta m n {f_0}^2 / \left(A \mu_q^{1/2} \rho_q^{1/2} \right) \quad (1)$$

in this formula, the change in the oscillation frequency (Δf) is equal to minus the change in interfacial mass (Δm) per unit area (A) times a constant. Thus the frequency decreases as the mass increases. The constant is evaluated with knowledge of the oscillation frequency of the fundamental mode of the QCM (f_0), the overtone number (n), the density of quartz and the shear modules of quartz.

For AT-Cut quartz wafers:

$$\Delta f = -2.3 \times 10^6 {f_0}^2 \Delta m / A \quad (2)$$

In this paper, ionic iodine in sample solution is converted into free iodine. Free iodine is then extracted into the carbon tetrachloride phase. The frequency of the crystal is decreased when free iodine is adsorbed on the gold electrodes of the crystal from the carbon tetrachloride solution.

3. Materials and methods

3.1. Apparatus and reagents

A QCM TTL-IC oscillator was made in this laboratory. Parameters of the circuit were as follows: impelling voltage: 2.6 V, crystal current: 1.76 mA. A universal frequency counter (CN3165, Sampo Technology Corp, Taiwan) was used to record the oscillating frequency of the crystal. Block diagram of the measuring apparatus was as Fig. 1.

Piezoelectric quartz crystal (PQC): AT-Cut, 9 MHz, diameter of the crystal: 12 mm, diameter of the electrodes (silver) on crystal: 6 mm (Beijing 707 factory, PR China).

Potassium iodide and potassium iodate were of spectrum regent grade (Sigma, USA). H_2O_2, sulphuric acid and other chemicals were of analytical regent grade. Deionized water was prepared with Milli-Q Labo (Millipore Corp., USA).

Samples of foodstuffs were procured from the local market. The samples were dried at 70°C and then ground and stored until analysis.

3.2. Standard reference materials (SRMs)

The standard reference material purchased from the National Center of Standards Materials Research of China [GBW(E)080235] has acertified value for content of iodine (200 mg/L, ±0.01). The GBW(E)080235 was used in this study to ensure that procedures of the methods (including QCM and gas chromatographic method) were under strict analytical control.

3.3. Gold plating of silver electrodes

Dirt on the electrodes of PQC was cleaned by 5# coated abrasive, and the PQC was washed with water and acetone, respectively. Gold plating of silver electrodes was finished by sputtering in vacuum (ion flow: 10 mA, time of sputtering: 3 min, decrease of frequency after sputtering: 20–45 kHz).

3.4. Standard curve and determination method

0.1308 g KI was weighed out, transferred to 1000 ml volumetric flask, and diluted to volume with deionized water. The iodine concentration of the stock standard solution was 100 mg/l.

Working standards for determination were prepared in the range of 0.01–0.50 mg/l by diluting standard stock solution with deionized water.

A 4 ml aliquot of working standard solution was pipetted into a 125 ml separating funnel, 3 ml of 3% (w/v)

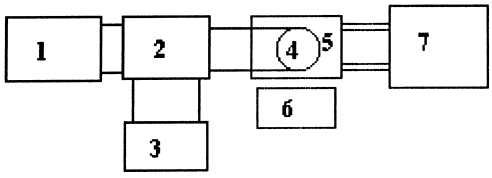

Fig. 1. Block diagram of the measuring apparatus 1. D.C. potentiostat, 2. TTL oscillator, 3. digital counter, 4. PQC, 5. measuring cell, 6. magnetic stirrer, 7. thermostat.

H_2O_2, 3 ml of 3 mol/L H_2SO_4 and 10 ml CCl_4 were added. After shaking for ca. 3 min and phase separation (3–5 min), the organic layer was transferred to the detection cell with a piezoelectric quartz crystal with frequency F_1. After adsorbing for 10 min under stirring up, the crystal frequency (F_2) was recorded. A standard curve $\Delta f = F_1 - F_2$ versus concentration of iodine in aqueous solution was constructed (Fig. 2).

After determination, the crystal was washed with 1 + 30 (V + V) ammonia for 5–10 min, then with deionized water to restore the original electrode frequency. Afterwards, the crystal can be used for next determination.

3.5. Sample determination

Solid samples of foodstuffs were treated according to the incineration method posed by Mahesh, Deosthale and Narasinga Roa (1992). Ashing was carried out in two stages, first with KOH and then with $ZnSO_4$.

Liquid samples such as beverage, blood and urine were treated by oxygen flask combustion method. The absorbing liquid was a mixture liquid of 10 ml of 0.1 mol/L NaOH and 1 ml of 1% $NaHSO_4$.

After the sample solutions were prepared, following determination steps of the samples were the same as that of working standards.

3.6. Gas chromatographic method used as comparison method (Mitsuhashi & Kaneda, 1990)

Iodide was oxidized to free iodine. Liberated iodine was reacted with 3-pentanone to form 2-iodo-3-pentanone, extracted into *n*-hexane and then determined by gas chromatography with an electron-capture detector. The instrumentation conditions are as follows: Pye-Unicam 204 GC equipped with a ^{63}Ni source electron-capture detector. GC column: 2 m × 3 mm id glass column packed with 10% DEGC and 1% H_3PO_4 on 60–80 mesh Chromosorb W HP. Operating temperatures: injection port: 180°C, column oven: 140°C, detector: 260°C. Nitrogen carrier gas: flow rate, 30 ml/min.

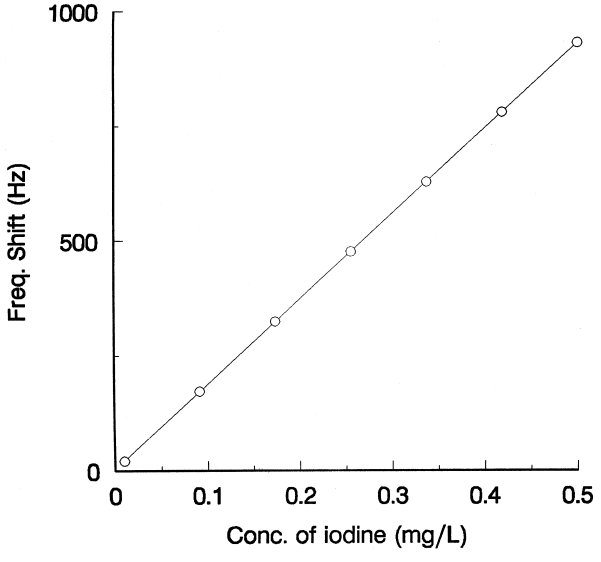

Fig. 2. Standard curve.

4. Results and discussion

4.1. Working conditions of the QCM method

4.1.1. Relationship between frequency shift of the QCM and adsorption time in CCl_4.

Fig. 3 shows the frequency shift of the QCM versus adsorption time relationship on different concentration of iodine in CCl_4. We can see that $d\Delta F/dt$ increases with increasing iodine concentration. So, for different iodine concentration, different adsorption time should be used. When the concentration is less than 3.80 mg/l, the time is 10 min, and 5 or 3 min for higher concentrations.

4.1.2. Solvent effect

Adsorbing of iodine on crystal in different solvents such as chloroform, isopropyl ether, *n*-heptane, carbon tetrachloride, etc., has been investigated (Table 1). From results, the frequency shifts of the crystal due to iodine adsorption are high in chloroform, *n*-heptane, CCl_4. But in oxygen-containing solvents such as alcohol, acetone and isopropyl ether, the frequency shift are rather low and $d\Delta F/dt$ is low too. The frequency shift is especially small in acetone.

4.1.3. Extraction conditions.

1. Extraction time: Speed of extraction is fast. The extraction reached its equilibrium within less than 1 min. In this paper, the extraction time of 3 min was used.

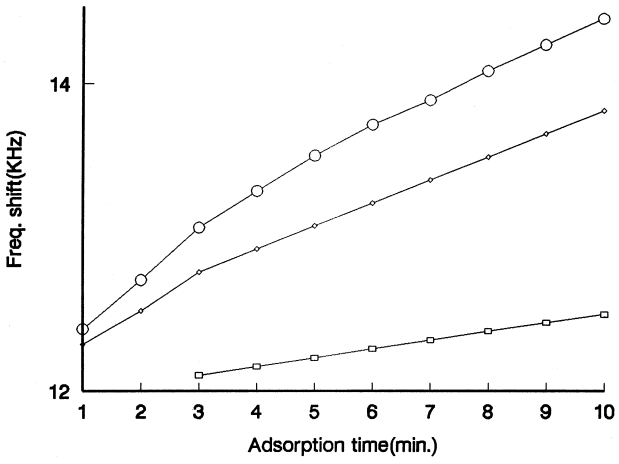

Fig. 3. Frequency shift–adsorption time relation on different concentration of iodine in CCl_4 phase: –O– 2.19 mg/l iodine; –◇– 1.33 mg/l iodine; –◇– 0.635 mg/l iodine.

2. Volume ratio of extracting solvent: The volume of CCl_4 was fixed at 10 ml. By changing the volume of water phase the volume ratio effect on iodine determination was studied. Results proved that determination results were not affected from 1:2 to 2.5:1 of ratio of water phase versus organic phase.

4.1.4. Restoration of the crystal

Different restoring regents are investigated (Table 2). From results, the free iodine adsorbed on the crystal can be removed by different solutions, such as: NaOH, Na_2CO_3, $NaHSO_3$ solution or ammonia, respectively, under proper restoration time and concentration condition to restore the frequency of the crystal. But NaOH solution can destroy the crystal to make the frequency increase, so it can not be used as a restoration reagent.

4.2. Specifications of the QCM method

4.2.1. Linear range of frequency shift versus concentration relationship

The relationship of frequency shift (ΔF) and concentration in working standard solutions had been investigated according to the method described in Materials and methods. In the range of 0.01–0.50 mg/l, the relationship is linear.

$$\Delta F(\mathrm{Hz}) = 2 + 1858\mathrm{C}\,(\mathrm{mg/l}) \quad \gamma = 0.9998$$

Stirring up has significant effect. When the solution is not stirred up, a narrow linearity range is observed, the sensitivity is rather low and about 1/3 of the sensitivity under stirring up (250 rpm).

4.2.2. Detection limit and recovery

The detection limit of the QCM method for iodine in aqueous solution was 0.0005 mg/l at a signal-to-noise ratio of 3 (the noise was 1 Hz). A recovery test was performed through adding iodine of different concentrations to the food sample. The results are given in Table 3. The recoveries of iodine were found to be in the range of 93.2–101.1% with a mean and standard deviation of $96.9 \pm 3.2\%$.

4.2.3. Effects of coexistent ions

Interfering effects of common ions for the determination of 0.28 mg/l I^- have been investigated. The results are shown in Table 4. When the common interference ion was not added to sample solution, the frequency shift caused by free iodine was 520 Hz. From the results, the frequency shift when most of common interfering ions was added to 0.28 mg/L I^- solution was also equal about to 520 Hz. So, no significant interferences were caused by anions such as Cl^-, F^-, NO_3^-, SO_4^{2-}, PO_4^{3-} and cations such as K^+, Na^+, $Ca2^+$, Mg^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Bi^{3+}. But for Br^- , it gives positive interference. When the concentration of Br^- was 2.9×10^{-6} mol/l in the 0.28 mg/L I^- solution, the

Table 1
Effect of solvent on the frequency shift of the crystal[a]

Solvent	Frequency shift (Hz)
Carbon tetrachloride	460
n-Heptane	570
Chloroform	520
Ethanol	287
i-Propyl ether	142
Acetone	21

[a] Iodine concentration: 0.25 mg/l.

Table 3
Recovery of iodine on the different concentrations in sample[a]

Iodine added (μg/kg)	Iodine found (μg/kg)	Recovery (%)
16.6	15.7	94.6
36.5	36.9	101.1
63.4	62.3	98.3
88.2	82.2	93.2
114.0	111.2	97.5

[a] Iodine was added to the sample in the form of KI.

Table 2
Restoration of the detector

Oscillation frequency (Hz)			Restoration		
Before adsorption	After adsorption	After restoration treatment	Agent	Concentration (mol/l)	Time (min)
8 992 250	8 992 140	8 992 260	NaOH	0.1	2
8 992 430	8 992 290	8 992 440	Na_2CO_3	0.5	5
8 777 760	8 777 505	8 777 765	Na_2CO_3	1.0	3
8 992 515	8 998 100	8 992 515	NH_3	1:1	5
8 993 305	8 993 135	8 993 300	$NaHSO_3$	1%	10
8 992 250	8 992 135	8 992 201[a]	$NaHSO_3$	1%	5
8 776 855	8 776 690	8 776 855	NH_3	1:30	10

[a] Incomplete restoration.

total frequency shift was 970 Hz that is largely higher than 520 Hz causing by free iodine absorbing.

4.2.4. Reproducibility of the QCM method used by different laboratories

For investigating the reproducibility of the QCM method used by different laboratories, we used the QCM method in three analytical laboratories to determine iodine content of same samples. The name of the laboratories is shown as follow: (1) analytical laboratory, new materials research institute of Hunan University (HU); (2) chemical research institute of Hunan Normal University (HNU); (3) instrumental analysis center of Hunan Health and Anti-epidemic Station (HHAS). Furthermore, the standard reference material [GBW(E)080235] was analyzed to control analytical quality. The results are shown in Table 5. The total C.V. of the analytical results of three laboratories was smaller than 4.1%.

Table 4
Effect of other ions for the determination of 0.28 mg/l I

Ion	Compd added	Concentration (mol/l) added	ΔF (Hz)
–	–	–	520[a]
K^+	KCl	2.0×10^{-4}	530
Na^+	$NaNO_3$	2.0×10^{-4}	530
Ca^{2+}	$CaCl_2$	2.0×10^{-4}	510
Mg^{2+}	$MgSO_4$	4.0×10^{-4}	530
Cu^{2+}	$CuSO_4$	1.6×10^{-5}	516
Zn^{2+}	$ZnSO_4$	1.6×10^{-5}	505
Co^{2+}	$CoCl_2$	1.7×10^{-5}	535
Ni^{2+}	$NiSO_4$	1.7×10^{-5}	505
Fe^{2+}	$(NH_4)_2Fe(SO_4)_2$	1.8×10^{-5}	540
Cd^{2+}	$CdCl_2$	1.2×10^{-5}	520
Pb^{2+}	$Pb(NO_3)_2$	1.0×10^{-4}	530
Fe^{3+}	$FeNH_4(SO_4)_2$	6.6×10^{-4}	511
Bi^{3+}	$Bi(NO_3)_3$	4.8×10^{-5}	545
F^-	NaF	1.4×10^{-4}	540
Cl^-	NaCl	1.0×10^{-4}	520
PO_4^{3-}	K_3PO_4	1.0×10^{-4}	550
Br^-	KBr	2.9×10^{-6}	970[b]

[a] None of other ions was added into the test solution.
[b] 4445 Hz in 2.9×10^{-6} M KBr solution containing no iodide.

4.3. Applicability

Using the QCM method, real food samples and body fluids were analyzed. Liquid samples were treated using oxygen bottle decomposition and solid samples were treated using alkaline dry ashing. The results are shown in Table 6. A gas chromatographic (GC) method (Mitsuhashi, 1990) is used as a contrast method to compare. For accuracy, each sample was assayed ten times. V.C. of determination was 1.3–4.3%.

In iodized salt, iodine normally exists in the form of iodate. So, when we determined the content of iodine in the iodized salt, the sample treatment was completed according to the principle of following reaction equation:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \quad (3)$$

Salt samples (100 mg) were transferred to a 10 ml volumetric flask and dissolved with 10 ml deionized water. 4 ml aliquot of sample solution was pipetted into 125 ml separating funnel, 2 ml 5% (W/V) KI, 1 ml H_3PO_4 and 10 ml CCl_4 were added. After shaking for ca. 3 min, and phase separation, the organic layer was transferred to the detection cell with a PQC and to determine. Following determination steps were the same as that mentioned in Materials and methods. The determination results of iodized salt samples are shown in Table 7.

Estimation of the iodine content of foods is beset with the difficulties of destruction of complex organic matter and quantitation of the iodine at ultra-trace levels. Therefore, the sensitive method to determine iodine in food is required. Now, the colorimetric methods based on the Ce–As–I catalytic reaction and derivative gas chromatography are used most often. However, inhibitors of the catalytic reaction exit (Ke, Thibert, Walton & Soules, 1973) and gas chromatography needs complex derivation procedures. These disadvantages limited the application of the methods. In contrast, the QCM method has more advantages such as simple, sensitive and anti-interference over the GC and the kinetic assay.

Table 5
Different laboratories results[a]

Sample no.	Laboratory results (μg/100 g)			Total mean ± SD	Total C.V. (%)
	HU	HNU	HHAS		
1	27.3 ± 0.72	26.7 ± 0.87	27.8 ± 0.21	27.3 ± 0.66	2.4
2	4.70 ± 0.19	4.54 ± 0.21	4.81 ± 0.09	4.68 ± 0.17	3.6
3	68.4 ± 1.27	70.2 ± 0.87	68.7 ± 0.91	69.1 ± 1.03	1.5
4	20.1 ± 0.87	21.6 ± 0.94	20.7 ± 0.74	20.8 ± 0.85	4.1
5	12.4 ± 0.47	13.1 ± 0.57	12.0 ± 0.37	12.5 ± 0.48	3.8
SRNMs (mg/l)	202.2 ± 2.74	199.5 ± 3.27	201.7 ± 2.97	201/1 ± 3./0	1.5

[a] No. of analyses is five.

Table 6
Iodine content of food samples

Sample	QCM method		GC method	
	Mean ± SD (μg I per 100 g)	C.V. (%)	Mean ± SD (μg I per 100 g)	C.V. (%)
Milk	14.7 ± 0.61	4.1	15.1 ± 0.57	3.8
Egg (hen)	63.4 ± 0.81	1.3	63.0 ± 2.39	3.8
Tomato	2.10 ± 0.03	1.4	2.03 ± 0.05	2.5
Potato	1.41 ± 0.06	4.3	1.45 ± 0.04	2.8
Apple	7.91 ± 0.10	1.3	7.58 ± 0.13	1.7
Serum (μg/100 ml)	3.10 ± 0.09	2.9	3.15 ± 0.11	3.5
Urine (μg/100 ml)	41.2 ± 0.58	1.4	40.5 ± 0.43	1.1
SRMs (mg/l)	196.5 ± 4.20	2.1	198.7 ± 5.13	2.6

Table 7
Iodine content of iodized salt

Sample no.	No. of analyses	Mean ± SD (μg I per g)	C.V. (%)
1	5	41.2 ± 0.91	2.2
2	5	42.3 ± 0.87	2.1
3	5	23.7 ± 0.76	3.2
4	5	19.8 ± 0.81	4.1
5	5	24.4 ± 0.67	2.7

5. Conclusion

The QCM method described here is a simple and sensitive procedure for determining iodine in foodstuffs. Its anti-interference ability for common anions and cations make it more advantageous than other analytical methods.

Acknowledgements

This work was supported by the Natural Science Foundation of China.

References

Alder, J. F., & McCallum, J. J. (1983). *Analyst, 108,* 1169.

Baker, H. J. (1977). Gas–liquid chromatographic determination of total inorganic iodine in milk. *Journal of the Association of Official Analytical Chemists, 60*, 1307–1309.

Curtis, A. R., & Hamming, P. (1982). *Journal of the Association of the Official Analytical Chemists, 65,* 20.

Dellavalle, M. E., & Barbans, D. M. (1984). *Journal of Food Protection, 47,* 678.

Fisher, P. W. F., L'Abbe, M. R., & Giroux, A. (1986). Colorimetric determination of total iodine in foods by As–Ce-catalysed reduction of Ce^{4+}. *Journal of the Association of Official Analytical Chemists, 69*, 687–689.

Guilbault, G. G. (1982). *Analytical Proceedings, 19,* 68.

Ke, P. J., Thibert, R. J., Walton, R. J., & Soules, D. K. (1973). *Microchimica Acta*, 569–581.

Lauber, K. (1975). Iodine determination in biological materials. Kinetic measurement of the catalytic activity of iodide. *Analytical Chemistry, 47*, 769–771.

Mahesh, D. L., Deosthale, Y. G., & Narasinga Rao, B. S. (1992). A sensitive kinetic assay for the determination of iodine in foodstuffs. *Food Chemistry, 43*, 51–56.

Mitsuhashi, T., & Kaneda, Y. (1990). Gas chromatographic determination of total iodine in Food. *Journal of the Association of Official Analytical Chemists, 73*, 790–792.

Moxon, R. E. D., & Dixon, E. J. (1980). Semi-automatic method for the determination of total iodine in food. *Analyst, 105*, 344–352.

National Research Council (1980). Recommended dietary allowances (9th ed). Washington, DC: National Academy of Sciences.

Sauerbrey, G. (1959). Verwendung von schwingquarzen zur wagung dunner schichten und zur mikrowagung. *Zeitschrift für Physik, 155*, 206.

Talbot, J. M., Fisher, K. D., & Carr, C. J. (1976). A review of the effects of dietary iodine on certain thyroid disorders. Bethesda, MD, PB262: Life Sciences Research Office, Federation of American Societies for Experimental Biology.

Thompson, D., Lee, S., & Allen, R. (1983). Differential pulse polarographic determination of iodine in foods and nutritional products. *Journal of the Association of Official Analytical Chemists, 66*, 1380.