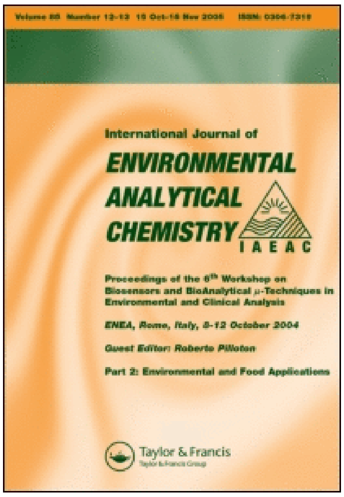

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Atomic Absorption Spectrophotometric Determination of Microgram Quantities of Copper in Tea After Solvent Extraction

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An atomic absorption spectrophotometric method is described for determining trace amounts of copper in tea. The method is based on the solvent extraction of the metal as tetraiodocuprate (I), from 2 M HCl solutions of tea samples which contain 12% (w/v) KI, into methylisobutyl ketone. The organic extracts, containing the ion-association complex of copper are atomized into an air-acetylene flame. The limit of detection is 1.14 $\mu g\,g^{-1}$ Cu.

KEY WORDS: Copper determination, atomic absorption spectroscopy, tea analysis, solvent extraction.

INTRODUCTION

Copper is an essential micronutrient for almost all organisms, particularly for humans, where an amount of about 2.0 mg has been estimated as a daily requirement.[1,2] It is known that tea contains some elements at trace levels. Therefore, it is desirable to determine the concentration of copper in tea from the health point of view.

Undoubtedly, atomic absorption spectroscopy is the most convenient, selective and sensitive technique for determining microgram quantities of copper. Flame[3,4] and carbon furnace[5] atomic absorption spectrophotometric methods were devised and used by independent workers to determine trace amounts of copper in tea and tea infusions, respectively. In the flame methods the tea samples were wet or dry ashed, and the resulting ash solutions were atomized into an air-acetylene flame. In the carbon furnace atomization method, the tea infusions were prepared by steeping the tea samples in 100 ml of boiling water for 5 min, filtering followed by atomizing 5 μl aliquots of the tea infusions in the carbon tube atomizer.

A close examination of the chemistry of copper revealed that ligands such as halides, cyanide and thiocyanate form the following complexes with Cu(II) ions[6,7] in aqueous solutions $[CuX_4]^{3-}$, $[Cu(CN)_4]^{3-}$ and $[Cu(SCN)_4]^{3-}$, respectively.

Preliminary studies of the author[8] revealed that copper can be extracted as iodide complex from acid solutions containing 12% (w/v) potassium iodide, into methylisobutyl ketone (MIBK). The organic extracts containing the ion-association complex of copper were then atomized into an air-acetylene flame. The proposed method is based on this technique, which was fully established after obtaining the optimum conditions for analysis. The acid recovery for copper was 95%.

EXPERIMENTAL

Apparatus

A Varian Model AA-475 double-beam atomic absorption spectrophotometer, equipped with a deuterium lamp background corrector was used with an air-acetylene flame. The resonance line at 324.7 nm from a copper hollow cathode lamp (Varian) was employed with a slit width of 0.2 nm and scale expansion ×2 on the spectrophotometer. The lamp current was 4 mA and the flow-rates of air and acetylene were 7.0 l min^{-1} at 60 psi and 1.5 l min^{-1} at 12 psi, respectively. A Berghof Pressure Digestion System, Model-TU-Regulator was employed for dissolving the tea samples, using conc. HNO_3 at 125°C for about 2 h.

Reagents

Analytical reagent grade reagents were used.

Standard copper nitrate solution A ($1000\,\mu g\,ml^{-1}$ of copper). Dissolve 1.00 g of copper metal in 30 ml (1 + 1) conc. HNO_3 and dilute to 1 l, using double-distilled de-ionized water.

Standard copper nitrate solution B ($1\,\mu g\,ml^{-1}$ of copper). Prepare this standard solution daily, by appropriate dilutions of the standard copper solution A, using 2 M HCl for dilution.

Potassium iodide solution, 40% (w/v). Prepare daily a solution containing 40% (w/v) of KI in 2 M HCl.

Materials

Ten international commercial tea brands were selected for determining their copper contents. Samples of these ten brands were purchased at food markets and analyzed according to this proposed method.

Analysis of the tea samples

Two analytical approaches were employed in preparing the tea samples for analysis by the proposed method.

a) Solvent extraction without dissolving the sample To 500 mg of dry tea sample in a 100-ml beaker, add 60 ml 2 M HCl. Cover the beaker with a watch glass and boil for 20 min on a water bath. Cool and then filter the acid extract into a separatory funnel. Wash the funnel filter with 5 ml 2 M HCl and then make up the volume to 70 ml, using the 2 M HCl (1st acid extract). Add another 60 ml of 2 M HCl to the tea residue in the beaker and repeat the procedure, collecting the extract in a second separatory funnel (2nd acid extract). Add 30 ml of 40% (w/v) of KI solution to both separatory funnels, and then pipette 10 ml of MIBK into each one of them. Shake for about 1 min and then allow the two layers to separate. Drain off the aqueous layers and discard them. Transfer the organic layers into 15-ml stoppered bottles. Atomize the organic extracts which contain the ion-association complex of copper, into an air-acetylene flame, using the given instrumental settings. Read the copper contents of the tea samples from the calibration graph of the metal.

b) Solvent extraction after dissolving the sample in a pressure vessel To 500 mg of tea sample in the pressure vessel, add 30 ml conc. HNO_3 and secure the lid tightly. Heat the vessel for about 2 h at 125°C and then leave to cool to room temperature. Transfer the dissolved sample into a 100-ml beaker and heat till dryness. Dissolve the residue in 50 ml 2 M HCl and transfer into a separatory funnel. Wash with 10 ml 2 M HCl and then make up the volume to 70 ml, using the 2 M HCl. Add 30 ml of 40% (w/v) of KI solution to the separatory funnel and continue as described above.

Preparation of calibration graphs

Pipette 0, 5, 10, 15, 20 and 25 ml of the copper standard solution B (1 $\mu g\,ml^{-1}$ Cu) into separate 250-ml separating funnels. Make up the volume to 70 ml. using the 2 M HCl and continue as described above. Atomize the organic extracts of these copper standards (0–2.5 $\mu g\,ml^{-1}$ Cu) and then draw the calibration graph.

RESULTS AND DISCUSSION

The resonance line at 324.7 nm from the copper hollow-cathode lamp was employed to construct calibration graphs for 0.0–2.5 $\mu g\,ml^{-1}$ of copper to determine the copper contents of the samples, by atomizing the copper standards and measuring absorbances versus concentration, followed by atomizing and measuring the absorbances of the MIBK extracts of the samples. The background corrector was switched on during all runs to correct any molecular absorption and/or scattering of light which might occur in the region of the 324.7 nm resonance line.

The calibration graphs were straight lines through the origin. The concentration of copper which gives 1% absorption was 0.01 $\mu g\,ml^{-1}$ Cu. Samples of ten tea brands were analyzed according to the proposed method, using the two approaches. The results are shown in Table I. The rel. S.D. of the method is 2.2%. The limit of detection is 1.14 $\mu g\,g^{-1}$ Cu, calculated as twice the standard deviation for 10 determinations of tea brand No. 3 (Table I). The probable error P, which equals 0.67σ—where σ stands for the standard deviation—is 0.40 $\mu g\,g^{-1}$ Cu.

TABLE I

Results for the determination of copper in tea.

Tea brand no.	Copper found ($\mu g\,g^{-1}$ Cu)			
	Approach (*a*)			
	1st extract	2nd extract	Total	Approach (*b*)
1	30.0	4.00	34.0	32.6
2	31.0	6.00	37.0	36.0
3	22.1[a]	3.40[a]	25.5[a]	25.0
4	23.5	6.50	30.0	30.0
5	22.0	6.00	28.0	27.6
6	26.0	8.00	34.0	35.0
7	34.0	5.50	39.5	40.0
8	29.0	9.00	38.0	37.4
9	26.6	13.6	40.2	39.0
10	30.0	6.40	36.4	35.0

[a] Average of 10 determinations. Other quoted results are the average of 2 determinations.

A set of 10 sample solutions containing 2.0 $\mu g\,ml^{-1}$ Cu was subjected to the proposed method, to verify the efficiency of the solvent extraction of the method. The MIBK extracts containing the iodide complex of copper were shaken with a 10 ml portion of a (1 + 1) mixture of conc. HNO_3 and conc. HCl in separatory funnels, in order to destroy the copper complex. The metal was back-extracted into the aqueous phase. The average of copper amounts recovered was 1.9 $\mu g\,ml^{-1}$ Cu, which indicated that the acid recovery for copper is 95%, using the proposed method.

It is known that copper(II) forms an iodide complex in acid solutions containing iodide.[6,7] The proposed method depends on the formation of tetraiodocuprate(I), $[CuI_4]^{3-}$, in 2 M HCl containing 12% (w/v) KI, which can be extracted into MIBK as ion-association complex. The stability of the ion-association complex was investigated in a way similar to the study of the ion-association complexes of lead and cadmium.[9] A set of 3 copper standards (2.5 $\mu g\,ml^{-1}$ Cu) was atomized into the air-acetylene flame, and the absorbance was read at varying times after the extraction. The results are shown in Figure 1. It is clear that the ion-association

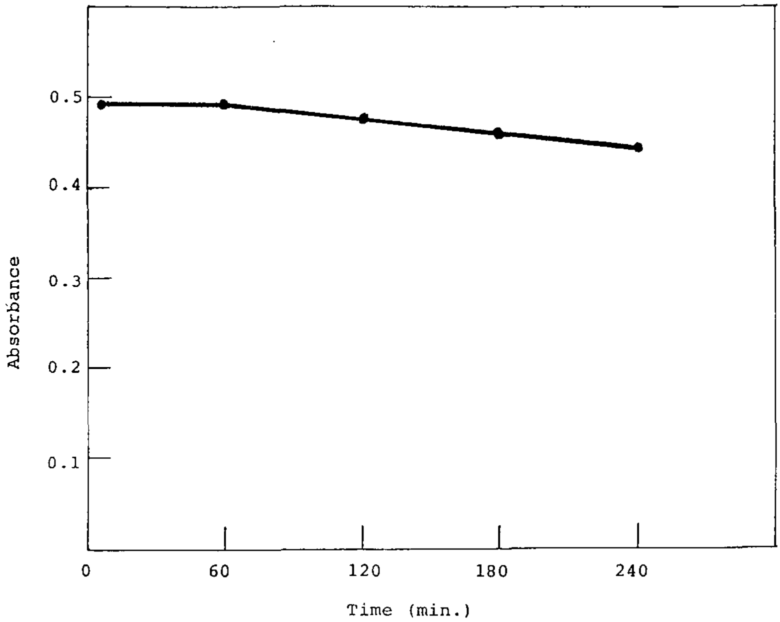

FIGURE 1 Stability of the ion-association complex of copper.

complex of copper is stable during 1 h. Subsequently, it starts to dissociate: after 4 h, there is a 10% reduction in the absorbance signal.

Under the experimental conditions used, an amount of copper greater than 30 mg gives a precipitate of CuI. Therefore, the method is free from this interference, because it is used for determining microgram quantities of copper.

Approaches *a* and *b*

The results in Table I show that the copper contents obtained by approach *a*, are in very good agreement with those obtained by approach *b*. This indicates that the proposed method, using either approach *a* or approach *b* is reliable. To verify the reliability of the results obtained in Table I, using both approaches *a* and *b*, the standard addition technique was carried out in analyzing samples No. 1, 5 and 9. The copper contents of these samples were 33.2, 27.5

and 40.5 $\mu g\,g^{-1}$ Cu against 34.0, 28.0 and 40.2 $\mu g\,g^{-1}$ Cu (Table I), respectively, using approach *a*; and 33.0, 27.0 and 39.4 $\mu g\,g^{-1}$ Cu against 32.6, 27.6 and 39.0 $\mu g\,g^{-1}$ Cu (Table I), respectively, using approach *b*. In other words, the proposed method is reliable and gives reproducible results.

Approach *a* is recommended as a routine method for the determination of copper in tea samples because it takes only about 1 h to prepare six tea samples for analysis, while approach *b* needs about 4–5 h in preparing the same number of samples (the heating block which was used by the author accommodates six pressure vessels). There is no doubt that approach *a* is not only a reliable, precise and accurate method, but also is a fast technique, which will be very advantageous particularly for people working in the tea industry.

Approach *a* certainly compares favourably with other known methods[3,4] used for determining microgram quantities of copper in tea, which are based on wet or dry ashing of the samples, followed by atomization of the resulting ash solutions into an air-acetylene flame. These methods have a lack of speed and lower precision and accuracy, which is attributed to matrix interference.

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