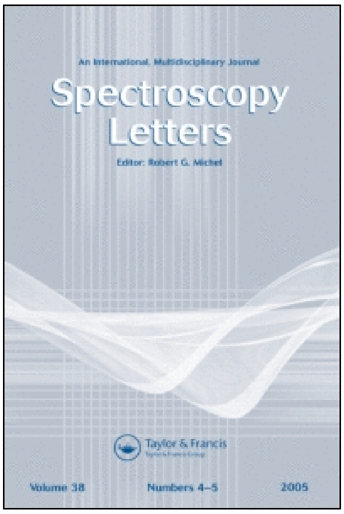

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

A Simple, Innovative Method for the Determination of Iodide by Using Gas-Phase Molecular Absorption Spectrometry After Volatile Species Evolution

Yixiang Duan[a]; Hanqi Zhang[a]; Xuemei Jiang[a]; Qinhan Jin[a]
[a] Department of Chemistry, Jilin University, Changchun, P.R. China

To cite this Article Duan, Yixiang , Zhang, Hanqi , Jiang, Xuemei and Jin, Qinhan(1996) 'A Simple, Innovative Method for the Determination of Iodide by Using Gas-Phase Molecular Absorption Spectrometry After Volatile Species Evolution', Spectroscopy Letters, 29: 1, 69 — 85

To link to this Article: DOI: 10.1080/00387019608001582

URL: http://dx.doi.org/10.1080/00387019608001582

SPECTROSCOPY LETTERS, 29(1), 69-85 (1996)

A SIMPLE, INNOVATIVE METHOD FOR THE DETERMINATION OF IODIDE BY USING GAS-PHASE MOLECULAR ABSORPTION SPECTROMETRY AFTER VOLATILE SPECIES EVOLUTION

Key Words: Iodide determination; Gas-phase molecular absorption; Method development; Chemical evolution; spectrometry.

Yixiang Duan, Hanqi Zhang, Xuemei Jiang and Qinhan Jin

Department of Chemistry, Jilin University, Changchun, 130023, P.R. China

ABSTRACT:

A simple, innovative method for the determination of iodide has been developed and described based on evolution of halogen gas and followed by gas-phase molecular absorption spectrometry (GPMAS) with a conventional hollow cathode lamp as primary radiation source. A convenient reaction vessel is designed for vapor generation and a flow-through absorption tube is used to replace the atomizer of a commercial atomic absorption spectrometer. Concentrated sulfuric acid is used as reaction agent to oxidize the iodide, and the produced iodine gas is carried into light path of the absorption cell. Measurement of the molecular absorption has been performed at wavelength 518 nm with a conventional Mg lamp. The detection limit for iodide attained is about 0.89 μg/ml and the relative standard deviation is usually less than 3% at the analyte concentration of 50 μg/ml. An interference study shows that the proposed method is selective and effective. The method has also been tested for real sample analysis.

INTRODUCTION

Although most metallic elements can be directly determined by conventional atomic absorption spectrometry (AAS), the application of the AAS for the determination of non-metallic elements has been limited based on the facts that most sensitive resonance lines of non-metallic elements are located in the vacuum ultraviolet region and appropriate hollow cathode lamps for the non-metallic elements are not readily available [1,2]. To overcome these problems, a series of research work have been pursued concerning the determination of non-metallic elements [3-6], including (1) use non-resonance line for absorption measurements; (2) modify instrument or use nitrogen-purged monochromator to reduce interference; (3) develop indirect methods for non-metallic element; (4) use gas-phase molecular absorption measurements instead of atomic ones. Among these, gas-phase molecular absorption spectrometry (GPMAS) is a relatively simple, less expensive and effective method, which has been used for the determination of halogens, sulfur [7-10], and even some hydride formation elements [11], provide these elements can form volatile species and their compounds have significant absorption in the ultraviolet and visible regions [12].

Syty and his coworkers developed several molecular absorption procedures for the determination of sulfur [7,8], and halogen [9], in which continuum sources, either hydrogen hollow cathode tube or deuterium arc lamp was used for sulfur and tungsten lamp was used for halogen. The detection limits for iodide and bromide by using oxidizing mixture were reported to be 14 μg/ml and 7 μg/ml, respectively. Cresser and Isaacson introduce the term, Gas-phase molecular absorption spectrometry (GPMAS) in 1976 [13]. More recently, a new method of molecular absorption for the simultaneous determination of sulfide and sulfur dioxide has been proposed by this laboratory [10], which gave 1 to 2 orders of magnitude improvements in detection limits for both sulfide and sulfur dioxide.

The present work investigates the possibility of improvements for the determination of halogen by using vapor evolution-molecular absorption. A typical halogen element, iodine, has been chosen for the test, and a conventional Mg hollow cathode lamp was used as an alternative source for primary radiation. The emission line of 518 nm from the Mg lamp was used for the absorption measurement. The research shows that iodide in aqueous solution can be rapidly, easily and precisely determined based on the oxidation and evolution of iodine followed by the molecular absorption. The detection limit obtained for iodine in this work is 0.89 μg/ml, which is about 15 times better than the literature value [9]. The proposed method is simple, effective, and applicable to real sample analysis.

EXPERIMENTAL

Instrumentation and Apparatus

The molecular absorption measurements for the evolved iodine were performed with Xintian (model WF-5) atomic absorption spectrometer, equipped with a strip-chart recorder and modified for gas-phase absorption measurements as illustrated in Figure 1. The modification consists of removing the original burner and replacing it with a 15-cm length, 0.7-cm i.d. Pyrex glass flow-through tubing with quartz end windows and an entrance port in the middle. This new absorption cell was supported by a holder to make the radiation source from HCL pass through

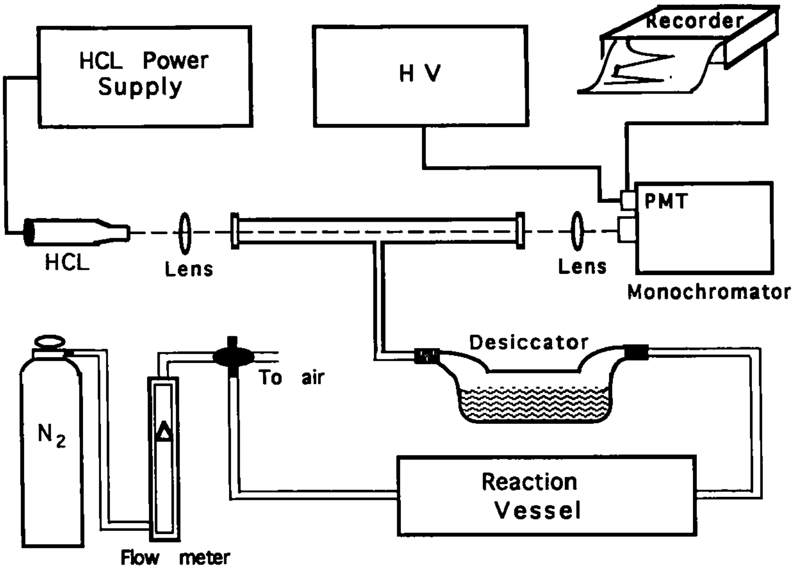

Figure 1. Experimental set-up for gas-phase molecular absorption spectrometry.

properly. The magnesium lamp was used as primary source, which has intense output at 518 nm, corresponding to the absorption peaks of iodine. The different components of the instrumental set-up are listed in Table 1, with some descriptions and specifications.

The sampling system consists of a reaction vessel and a desiccator. The sample apparatus used for evolution of iodine is shown in Figure 2. A 3-channel glass vessel provides efficient gas flow and sample vapor transport. The total volume of the reaction vessel is about 30 ml with a compact structure. The inner diameter of the main portion is about 18 mm. As shown in the Figure 2, the carrier gas (nitrogen) is introduced from a dispersion tube (central channel) and sweeps the evolved iodine gas into the absorption cell. A 3-way stopcock and a flow meter were installed in the gas channel (see Figure 1) to control and regulate the carrier

TABLE 1

Description and Specifications of the Major Components in the Experimental Set-up and Operating Conditions

Atomic absorption spectrometer	Commercially available WF-5 Model, manufactured by Guei-Zhou Xintian Optical Fine Instrument Factory, China.
Primary radiation source	Mg hollow cathode lamp, worked at 518 nm wavelength and 8 mA current.
Monochromator slit width	0.3 mm, with a slit height of about 1 cm.
Detection system	1P28 PMT, worked with a high voltage of about 800 V.
Read-out system	A commercial chart recorder, type 056, Hitachi Corporation
Reaction vessel	Three channel system made of Pyrex glass, built in the laboratory.
Desiccator	Concentrated H_2SO_4, analytical grade, held with a home-made glass vessel.
Absorption cell	A quartz or Pyrex glass tube, covered with quartz window in both ends, built in the laboratory.
Reaction solution	Concentrated H_2SO_4, analytical grade.
Reaction solution volume	3 ml.
Sample solution volume	1 ml.
Sample solution concentration	50 µg/ml
Reaction time	7 s.
Carrier gas flow rate	1.5 L/min.

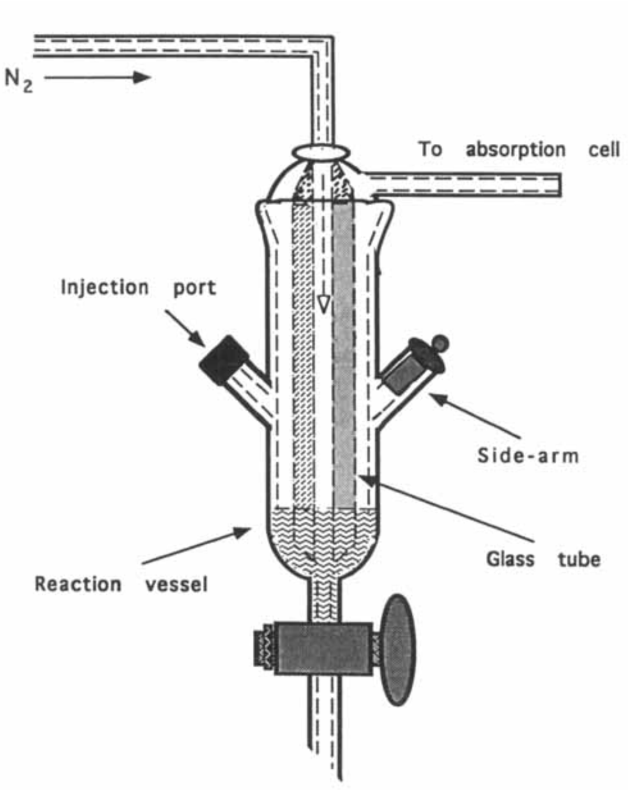

Figure 2. Apparatus for the evolution of iodine.

gas. A concentrated sulfuric acid held in a glass vessel (Figure 1) is used as desiccator to eliminate the residue water vapor from both reaction vessel and/or carrier gas and to improve the analytical performance. As we reported before [14,15], the addition of this desiccator will significantly increase signal intensity and reduce the noise level. The oxidizing solution is measured by a syringe and placed into the reaction vessel through the side-arm. A 1-ml Hamilton syringe is used to inject the iodide solution into the oxidizing solution through the rubber septum covering the injection port. Removal of spent reagent and replacement of fresh oxidizing solution is made rapid and convenient by a drain stopcock at the bottom of the reaction vessel and by a side-arm injection. The reaction vessel used here offers an apparent improvement over the apparatus reported in the literature [9]. It has a smaller volume and a compact structure.

Reagents

All chemicals used are of analytical grade or better. Water was distilled and deionized with a special device. Nitrogen is preferred as carrier gas though compressed air may also be used. Stock standard solution of iodine was prepared by dissolving analytical grade KI in distilled-deionized water. The accurate concentration of I^- was standardized by titration just before use. Working standard solutions were usually prepared daily by serial dilution of the stock solution with water.

Procedure

For the optimum conditions, a 3-ml aliquot of the oxidizing solution is introduced from the side-arm into the reaction vessel. The nitrogen flow rate is set at 1.5 L/min, and the 3-way stopcock was adjusted to let the carrier gas flow into air, then a baseline on the recorder is established. With the gas flow and the recorder on, a 1-ml aliquot of sample solution is injected through the injection port of the reaction vessel. After reacting for a certain time (usually defined as the reaction time), the 3-way stopcock is turned on to the channel which the carrier gas can flow into the reaction vessel and sweep the evolved iodine into the absorption cell. An absorption signal appears almost immediately on the chart-recorder, quickly reaches a maximum, and then fall off rapidly. As soon as the peak is recorded, the reaction vessel is emptied by switching the stopcock at bottom of the vessel, and then refilled with a fresh aliquot of oxidizing solution, which cause the recorder pen to return to its original base line for the next sample injection.

RESULTS AND DISCUSSION

Selection of Experimental Conditions for the Instruments

As reported in the literature [12], halogens have significant absorption bands at visible and even ultraviolet regions. A absorption band around 530 nm has been used for iodine measurement with a continuum primary source [9]. In the present work, an effort has been made to use acute line source instead of continuum source for molecular absorption measurement. Several hollow cathode lamps (HCLs), which have output (spectral emission lines) around 530 nm, have been examined. Among these, magnesium was found to give better radiation at wavelength of 518 nm, which is very close to the maximum absorption peak of the iodine, and was selected as analytical line for this work. With a 1-ml of 50 μg/ml sample solution and 3-ml reaction solution as well as a carrier gas flow rate of 1.5 L/min, HCL current influence on the signal intensity was examined from 6 to 12 mA. No significant influence was found. We choose 8 mA as HCL's working current throughout this project.

The selection of slit width for the spectrometer is based on the signal to noise ratio. Actually, there is no significant change on signal intensity from slit width 0.3 mm to 0.7 mm. However, the noise level increases with the slit width. Therefore, the better signal to noise ratio was obtained at slit width of 0.3 mm. Below this value, the signal intensity decreases rapidly. All the selected operating conditions for this work are listed in Table 1 unless otherwise stated.

Optimization of Iodine Evolution and Measurements

Volume and concentration of oxidizing solution: As one can imagine, the iodide can be oxidized by different concentrations of sulfuric acid solution.

However, the ability of the oxidation decreases with dilution. Although addition of some auxiliary oxidant to the diluted sulfuric acid solution may be helpful for enhancing the oxidizing ability, as suggested in the previous work [9], we found that the concentrated sulfuric acid give the best results for the iodide. In addition, the volume of the oxidizing solution also has significant effect for evolving iodine. The influence on the evolution of iodine of changing the volume was tested with 1.0 ml 50 μg/ml sample solution and carrier gas flow rate at 1.5 L/min. The relationship between the volume of oxidizing solution and the signal absorbance for iodine is plotted in Figure 3, which shows that in lower volume (< 2.0 ml), the absorbance increases with oxidizing solution volume. This means that in this case, the oxidation ability of the concentrated sulfuric acid is reduced by the dilution during mixing process with sample solution. This will certainly decrease the signal intensity. On the other hand, an extra oxidizing solution will dilute sample solution during reaction process and may also absorb some evolved iodine. Both of these effects will result in the decrease of absorbance. In this experiment, we found that the best volume for oxidizing solution is 3.0 ml.

Carrier gas flow rate: With the objective to find the optimum carrier gas flow rate, the N_2 flow rate was varied from 0.25 L/min to 2.1 L/min for repeated injection of 1.0 ml aliquots of 50 μg/ml solution into fresh 3.0 ml aliquots of the oxidizing solution contained in the reaction vessel. The results are shown in Figure 4. As can be seen, the flow rate over 1.5 L/min is not benefit for the absorbance. Much higher flow rate (over 2.1 L/min) has not been tested because it is not practical with present apparatus. The data in Figure 4 indicate that there is no significant effect on the analyte signal for the carrier gas flow rate from 1.5 to 2.1 L/min. Flow rates below 1.5 L/min tend to lower the absorbance and wider the peaks. Overall, the magnitude of the effect of carrier gas flow rate on the absorbance is remarkably small. Similar effects have also been reported earlier [9].

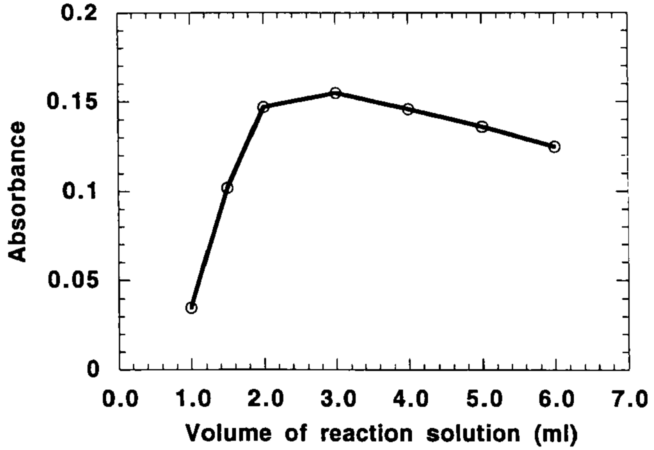

Figure 3. Reaction solution volume effect on the absorbance of iodine.

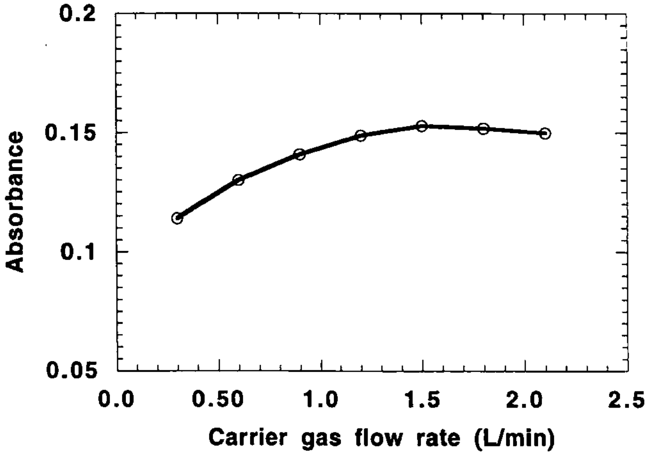

Figure 4. Carrier gas flow rate effect on the absorbance of iodine.

Reaction time (or accumulation time): It should be noted that the operation mode in this study is different from the previous studies [7-9]. As mentioned earlier, the operation in this work is in a pulsed mode. The evolved iodine vapor was collected and/or accumulated during the reaction. Definitely, this pulsed mode operation will increase sensitivity of the method. The time interval from the sample injection into the reaction cell to the carrier gas flow in by turn on the 3-way stopcock is defined as the reaction time or accumulation time. The effect of this time interval on the absorbance has been examined under the conditions provided in Table 1. The experimental results show that influence from reaction time is not so significant from 5 seconds to 30 seconds (see Figure 5). Below 5 seconds, the absorbance value tends to be lower, which demonstrate that oxidization reaction is not as fast as neutralization reaction does, as was done in our previous work [10,16,17]. Over 30 seconds, the absorbance value decreases slightly with the reaction time. A 7-s was selected as acceptable value throughout this work.

Analytical Characteristics

Based on the experimental conditions given in the Table 1, the detection limit for iodine by using GPMAP method has been evaluated. Here, the detection limit is defined as the concentration of analyte which gives a signal three times of the standard deviation of blank signal. Peak height was measured for the calculation of the detection limit. For eleven continuos injections into fresh 3-ml aliquots of reaction solution, the detection limit obtained was shown to be 0.89 μg/ml, which gives about 15 times improvement of the previous results [9]. Calibration curve (Figure 6) shows that the linear range can be obtained from 3 μg/ml to 500 μg/ml of iodine. Curvature toward the concentration axis is observed at higher concentrations.

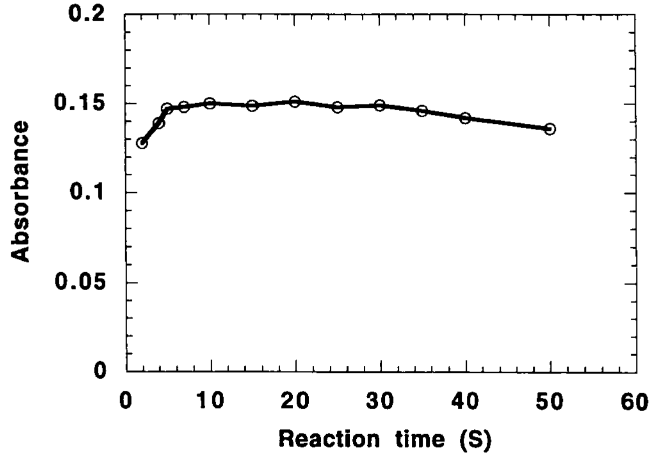

Figure 5. Reaction time (or accumulation time) effect on the absorbance of iodine.

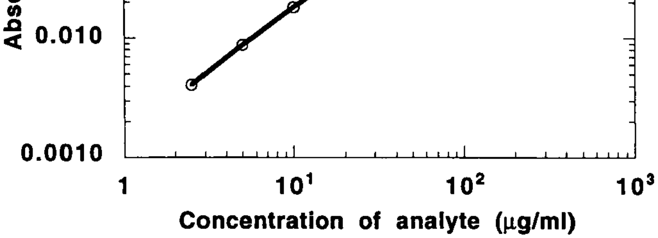

Figure 6. Calibration curve for the iodine.

Reproducibility was also examined by using 1-ml aliquots of standard iodide solution injected repeatedly into fresh aliquots of reaction solution. Based on at least 10 replicates, the reproducibility observed with 50 μg/ml iodide solution is pretty good. Relative standard deviation (RSD%) is less than 3%. It should be pointed out that successive injections of sample solution into the same aliquot reaction solution were proved to be unacceptable due to the decreasing trend in the resulting absorbance and lack of signal reproducibility.

Selectivity and Interference

Many potential matrix effects rose from concomitant ions in the sample solution should be avoided by the vapor generation and separation of the volatile molecular iodine. However, as we expected, matrix or concomitant ion interference may occur in the chemical generation process itself. To evaluate the extent of such possible interference, several anions and cations were tested for the potential interference upon the evolution of I_2 and its absorbance in the gas phase at 518 nm. The absorption signal due to a 1-ml aliquot of 50 μg/ml I^- was compared to the absorption signals of 1-ml aliquots of mixtures 50 μg/ml in I^- and certain ratios in the test ions. All injections were made into fresh oxidant in the reaction vessel. The results, given in Table 2, shows the error range based on at least five repeated injections of all solutions. As can be seen from the Table 2, the proposed method is selective for iodide among many concomitants. No significant interference was found for Cl^-, SO_3^{2-}, SCN^-, Ca^{2+}, Cu^{2+}, Zn^{2+} at concentration as high as 500 μg/ml. Br- has no effect on the determination of iodine at the concentration of 50 μg/ml, and the error is less than 5% at the concentration of 250 μg/ml. Some other anions, CO_3^{2-}, NO_3^- and CN^-, do have effects on the absorbance of iodine at the concentration of 500 μg/ml, but with a error range less than 10%. The influence rose from Fe^{2+} may be due to its reduction property. When a large quantity of Fe^{2+}

TABLE 2

Selectivity and Tolerance Achieved in the Determination of 50 μg/ml Iodine

Interference ions tested	Interference ion amount added	Tolerance ratio achieved	Error range
Br-	50 μg/ml	1:1	< 3%
S^{2-}	50 μg/ml	1:1	< 3%
Fe^{2+}	100 μg/ml	2:1	< 5%
Br^-	250 μg/ml	5:1	< 5%
Cl^-	500 μg/ml	10:1	< 3%
SO_3^{2-}	500 μg/ml	10:1	< 3%
SCN^-	500 μg/ml	10:1	< 3%
Ca^{2+}	500 μg/ml	10:1	< 3%
Cu^{2+}	500 μg/ml	10:1	< 3%
Zn^{2+}	500 μg/ml	10:1	< 3%
CO_3^{2-}	500 μg/ml	10:1	< 10%
NO_3^-	500 μg/ml	10:1	< 10%
CN^-	500 μg/ml	10:1	< 10%

added into the solution, it may reduce the oxidation ability of the concentrated sulfuric acid. Besides all ions discussed above, some other cations, such as Ag, which are able to react with iodide and form precipitation, of course will change the concentration of the analyte and give a negative result. All of these effects should be taken into account in real sample analysis.

Recovery

To examine the reliability of the proposed method for the determination of iodide or iodine, we artificially make a solution which contains 50 μg/ml KI, 50 μg/ml Br^- and Fe^{2+}, 150 μg/ml NO_3^- and SCN^-, 500 μg/ml Zn^{2+}, Mg^{2+}, Cu^{2+} and

TABLE 3

Recovery of Iodine from Artificial Solutions

Sample No.	I^- added (μg/ml)	Coexistence ions (μg/ml)	I^- found (μg/ml)	Recovery (%)
1	50	50 μg/ml Br^-, Fe^{3+} 150 μg/ml NO_3^-, SCN^- 500 μg/ml Zn^{2+}, Mg^{2+}, Cu^{2+}, SiO_3^{2-}	49.2	98.4
2	50	50 μg/ml Br^-, Fe^{3+} 150 μg/ml NO_3^-, SCN^- 500 μg/ml Zn^{2+}, Mg^{2+}, Cu^{2+}, SiO_3^{2-}	51.4	102.8
3	50	50 μg/ml Br^-, Fe^{3+} 150 μg/ml NO_3^-, SCN^- 500 μg/ml Zn^{2+}, Mg^{2+}, Cu^{2+}, SiO_3^{2-}	51.8	103.6
Mean recovery (%)				101.6
RSD (%)				2.7

SiO_3^{2-}. The same analytical procedure was followed after injecting the artificial sample solution into the reaction vessel. Three sample solutions were tested, and the results obtained are listed in Table 3. The recoveries showed in Table 3 range from 98.4% to 103.6%, with a RSD of about 2.7. Considering the method precision discussed above, the recovery obtained from the artificial solution is satisfactory.

Application to Real Sample Analysis

To assess the analytical usefulness of the method in real samples, we applied it to the determination of iodide in a iodized salt. About 2-g NaCl sample was carefully weighed and dissolved in deionized water. The solution was transferred into a 100-ml volume flask and filled to mark with deionized water. The prepared sample solution was directly injected into the reaction vessel without any further treatment. To reduce some potential matrix effects, which may be risen from unknown components in the salt, a standard addition method was used for the determination of iodide. The result obtained shows that KI content in the salt is 1.32 mg/g, which is basically agree with the certificate value.

CONCLUSIONS

A simple, innovative method for the determination of iodine has been developed based on the vapor evolution and gas-phase molecular absorption measurements by using magnesium hollow cathode lamp as primary radiation source at wavelength of 518 nm. The results presented in this work confirm the idea that the use of GPMAS method enables the determination of halogen which can be evolved from solution samples. The proposed method is selective, efficient and much more sensitive than the one reported in the previous work [9]. The instrument used here is relatively simple and less expensive. The operation is easy to learn and handle. Possible improvements for the present system may include, (1) use on-line automatic sampling system instead of manual injection, which certainly will improve the precision of the measurements; (2) use integrated peak area instead of peak height for the calculation of analytical figure of merit. (3) choose varied HCLs and different emission lines to avoid possible spectral interference.

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Received: March 15, 1995
Accepted: April 27, 1995