GFAAS Determination of Chloride in Uranium Using AgCl Precipitation

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INTRODUCTION

The trace level assay of metallic and non-metallic constituents of nuclear materials forms an essential part of the chemical quality control program in nuclear fuel development. Analytical atomic absorption and emission spectroscopic methods suited for this purpose have been fully explored in our laboratory (1-5). The presence of some of these impurities, even at trace levels, can affect the fuel performance adversely, thus necessitating their sensitive and precise determination. Chloride is mainly picked up by fuels from chemical reagents and organic compounds used in fuel fabrication. The presence of halides at trace levels, due to their high reactivity, would result in early rupture of fuel cladding. The chloride content of fuel has stringent specifications of 15 and 20 ppm for pressurized heavy water reactor (PHWR) and fast breeder reactor (FBR) fuels, respectively (6). The principal emission lines of chloride and other non-metals lie in the vacuum ultraviolet (UV) region, necessitating special precautions to minimize intensity losses due to absorption in the air for their determination by conventional atomic emission spectroscopic methods (7). Atomic absorption spectrometric (AAS) methods reported for chloride determination are indirect due to the unavailability of chloride hollow cathode lamps (7). Some of these methods include measurement of copper concentration in samples by flame AAS, which was reported to be proportional to the

ABSTRACT

This paper describes a graphite furnace atomic absorption spectrometric (GFAAS) method for the direct determination of chloride in uranium. The method is based on an indirect approach of monitoring excess silver present in a uranium solution after precipitation of chlorine as AgCl. It was found that interference from other halides, i.e., Br⁻ and I⁻, could be overcome by prior addition of Cu²⁺ to the sample solution containing 15% (v/v) of ethanol. This removes Br⁻ and I⁻ due to the formation of insoluble cuprous salts. Using the optimized conditions of copper and ethanol addition, chloride can be determined in the concentration range of 0.5–50 ppm in uranium with a precision of $\pm 15\%$ in the presence of halides.

chloride content of the inorganic or organic samples (8), chloride in rain water using derivatization with phenyl mercury nitrate and determination by AAS (9), and precipitation of chloride as phenyl mercuric chloride and Hg determined by AAS (10). Other methods determine unreacted (11) or reacted silver (12,13) for obtaining chloride estimates. The methods commonly used in the determination of halogens include ion chromatography (14), pyrohydrolysis-potentiometry using ion selective electrodes (15–16), mass spectrometry and x-ray fluorescence spectrometry (17,18).

In the present study, GFAAS, known for its selectivity and good precision, is used for the indirect

determination of chloride in a uranium matrix. Chloride in uranium was determined without chemical separation of the major matrix. The interferences of Br⁻ and I⁻ on chloride determination were investigated and overcome by using copper as a masking agent.

EXPERIMENTAL

Instrumentation

A modular type Varian Techtron AA-6 atomic absorption spectrometer, equipped with a pyrolytically coated carbon rod atomizer (CRA-63) and deuterium lamp background corrector (BC-6), was used in the investigations. Details of the Ag determination in uranium are described elsewhere (1). The instrumental parameters for the determination of Ag using CRA-63 GFAAS are given in Table I.

TABLE I
Instrumental Operating
Conditions for Ag
Using CRA-63 GFAAS

Parameters	Values
Wavelength	328.1 nm
Spectral bandpass	0.5 nm
Lamp fill gas	Ne
Lamp current	5 mA
Flow rate	6 L/min

Preparation of Standard Solutions

High purity uranium oxide with Ag < 0.1 ppm and chloride < 0.25 ppm was used for preparation of the standards and the synthetic samples. A stock solution of uranium (250 mg/mL) was prepared by dissolving appropriate amounts of uranium oxide in con-

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concentrated nitric acid, followed by dilution with 0.1 M nitric acid. Stock solutions of 2 mg/mL of chloride, fluoride, and bromide were prepared from their respective sodium and potassium salts. Iodine stock solution of 2 mg/mL was prepared by dissolving iodine lumps in ethyl alcohol. Stock solutions of 2 mg/mL of silver and copper were also prepared in 0.1 M HNO₃ from the respective nitrates.

Sample Preparation

The present method of chloride analysis is based on the determination of excess silver present in a uranium solution after precipitation of chlorine as AgCl. The estimated range of silver was reported to be 0.002–0.04 µg/mL in aqueous solutions and 0.002–0.08 µg/mL using 20 mg/mL uranium standard solutions. Details of the sample preparation are given below.

(a) Effect of Alcohol on Chloride Estimation

A set of samples, in duplicate, containing 2.5 µg of chloride and varying amounts [0, 5, 10, 15, and 20 % (v/v)] of ethanol to which 20 µg of Ag was added, was brought to 5 mL volume with 0.1 M HNO₃. Each sample was centrifuged for 5 minutes and allowed to settle. A 100 µL amount of supernatant of each sample was diluted to 5 mL,

and 5 µL each analyzed for its silver content. Another set of samples in duplicate, having 1.2 µg of chloride and 4 µg of silver with 0 and 15% (v/v) ethanol, respectively, was prepared in a similar way and analyzed for its silver content. Details of the preparation and the chloride concentration of these samples are given in Table II.

(b) Effect of Other Halides on Chloride

A set of samples in duplicate was prepared containing 500 mg each of uranium and chloride, as well as varying amounts of bromide, iodide, copper, and ethanol [15% (v/v)]. Then, 20 µg of Ag was added and the volume made up to 5 mL with dilute HNO₃. The final samples were prepared using the same procedure as listed in (a) above. These samples were analyzed for silver to monitor the effect of bromide and iodide in the determination of chloride and the role of copper as a modifier. The effective concentration of U in the sample taken for analysis was 2 mg/mL and, hence, all uranium samples were analyzed using silver standards with a 2-mg/mL U concentration. Details of the preparations and the results are listed in Table III.

Procedure of Chloride Determination

To establish the range of analysis for the determination of Cl⁻ in actual samples, a set of synthetic samples was prepared. These samples consisted of fixed amounts, i.e., 500 mg of U, 25 µg each of bromide and iodide, and 50 µg copper in the form of Cu(NO₃)₂ solution to which varying amounts of chloride (in the range 0.5–25 µg) were added and the sample volume was made up to 5 mL with 0.1 M HNO₃. Aliquots of 1.0 mL and 2.5 mL of these samples were taken to which 0.75 mL ethanol [15% (v/v)] and 20 µg Ag as AgNO₃ were added. The total volume of the samples was made up to 5 mL with 0.1 M nitric acid. The resulting solution was stirred for 5 minutes and allowed to settle. A 100 µL amount of supernatant was taken out and diluted to 5 mL, then 5 µL of each of these samples was analyzed for its silver content. The chloride estimates of these samples are listed in Table IV.

Reference Samples

An amount of 1.12 g of uranium oxide (corresponding to 1 g of U) was dissolved in 6 M HNO₃ and brought to volume in 10 mL of 0.1M HNO₃. Then 1 mL and 2.5 mL aliquots of the reference sample having 15% ethanol were mixed with 50 µg of copper and 20 µg of silver. The respective samples were made up to 5 mL volume in 0.1M HNO₃, centrifuged for 5 minutes, and 100 µL of the supernatant was diluted to 5 mL with 0.1M HNO₃. A 5-µL amount of each of these samples was analyzed for its silver content. The chloride estimates of these samples are listed in Table V.

TABLE II
Effect of Alcohol Addition on Chloride Determination

Sample No.	Sample Volume (mL)	Chloride Added (µg)	Ethanol Added (% v/v)	Silver Added (µg)	Chloride Added (µg/mL)	^a Chloride Determined (µg)
1	5	2.5	0	20	0.10	0.50
2	5	2.5	5	20	0.46	2.30
3	5	2.5	10	20	0.48	2.40
4	5	2.5	15	20	0.49	2.45
5	5	2.5	20	20	0.42	2.30
6	5	1.2	0	4	0.04	0.2
7	5	1.2	15	4	0.23	1.15

* Average of two sample readings.

TABLE III
Effect of Bromide, Iodide, and Copper Addition on Chloride Determination

Sample No.	Sample Volume (mL)	Uranium Added (mg)	Ethanol Added (mL)	Chloride Added (µg)	Bromide Added (µg)	Iodide Added (µg)	Silver Added (µg)	Copper Added (µg)	^a Chloride Determined (µg)
A									
1	5	500	0.75	2	—	—	20	—	1.9
2	5	500	0.75	2	2	2	20	—	2.72
3	5	500	0.75	2	4	4	20	—	4.35
4	5	500	0.75	2	2	2	20	4	1.87
5	5	500	0.75	4	4	4	20	8	3.78
B									
1	5	500	0.75	2	2	2	20	4	1.86
2	5	500	0.75	2	4	4	20	8	1.82
3	5	500	0.75	2	10	10	20	20	1.84
4	5	500	0.75	2	20	20	20	40	2.05
5	5	500	0.75	2	25	25	20	50	1.90
6	5	500	0.75	10	10	10	20	50	9.8
7	5	500	0.75	25	25	25	20	50	23.4
C									
1	5	500	0.75	0.25	1	1	20	2	0.15
2	5	500	0.75	0.25	1	1	20	50	0.20
3	5	500	0.75	0.5	1	1	20	2	0.45
4	5	500	0.75	0.5	1	1	20	50	0.47
5	5	500	0.75	1	1	1	20	2	0.90
6	5	500	0.75	1	1	1	20	50	0.92

* Average of two sample readings..

TABLE IV
Results of Chloride Determination for Synthetic Samples Taken in Duplicate

Sample No.	Sample Volume (mL)	Uranium Added (mg)	Chloride Added in 5 mL (µg)	Br ⁻ & I ⁻ Added (µg)	Chloride Content (µg)		Ethanol (mL)	Cu Added (µg)	Ag Added (µg)	Chloride Content (µg)		Chloride Determined (µg)	RSD (%)
					1 mL ^a	2.5 mL ^b				1 mL ^a	2.5 mL ^b		
1	5	500	0.0	25+25	00.0	00.0	0.75	50	20	0.005	0.006	—	
2	5	500	0.5	25+25	0.10	0.25	0.75	50	20	0.089	0.222	0.44	15
3	5	500	1.0	25+25	0.20	0.50	0.75	50	20	0.180	0.445	0.90	12
4	5	500	5.0	25+25	1.0	2.5	0.75	50	20	0.910	2.24	4.5	10
5	5	500	10.0	25+25	2.0	5.0	0.75	50	20	1.880	4.62	9.3	9
6	5	500	15.0	25+25	3.0	7.5	0.75	50	20	2.790	N.D.	13.9	9
7	5	500	20.0	25+25	4.0	10.0	0.75	50	20	3.800	N.D.	19.0	8
8	5	500	25.0	25+25	5.0	12.5	0.75	50	20	4.720	N.D.	23.6	8

^a = Based on the analysis of 1 mL aliquots of chloride.

^b = Based on the analysis of 2.5 aliquots of chloride.

TABLE V
Results of Spiked Samples (in duplicate) for Chloride Determination

Sample No.	Chloride Concentration (ppm)		(%) RSD
	Expected	Determined	
1	4.0 ^a	3.8	12
2	26.5*	125.4	9

^a = Reported by pyrohydrolysis-spectrophotometric method based on 1 g of sample.

RESULTS AND DISCUSSION

Silver is one of the specified elements in nuclear materials and the determination of silver in UO_2 and $(\text{U}, \text{Pu})\text{O}_2$ matrices was reported earlier (1,2) from our laboratory. The method developed for the determination of chloride in a uranium matrix is based on the determination of unreacted Ag left behind in the solution after precipitation of chloride as AgCl. The reaction between silver and chloride in aqueous solution is as given below:

Part of the precipitated AgCl redissolves in aqueous solution since AgCl has a solubility of $0.9 \mu\text{g/mL}$ in water (19). This would bring $0.675 \mu\text{g}$ of Ag and $0.225 \mu\text{g}$ of chloride back into the solution resulting in an overestimation of the unreacted silver concentration which, in turn, would lead to an underestimation of chloride in the sample. The amount of unreacted silver gives the amount of silver that has reacted only if the solubility of AgCl in an aqueous medium can be made negligibly small. Under this condition, the chloride content of the sample is given by $(\text{Ag}_{\text{added}} - \text{Ag}_{\text{unreacted}}) / 3$. Hence, prior knowledge of the Ag concentration in a given sample is necessary for the precise determination of chloride.

Effect of Alcohol Addition

Ionic solids have low solubility in nonpolar solvents. Hence, the solubility of AgCl in water (polar solvent) can be reduced considerably by precipitating AgCl in a mixture of polar and non-polar solvents. The feasibility studies for chloride determination were carried out with the addition of ethanol at 0, 5, 10, 15, and 20% (v/v) in the sample (Table II). When samples were prepared with 0% ethanol, the chloride estimates had a nega-

tive bias, whereas the chloride estimates in the presence of ethanol (5, 10, 15, and 20%) were in good agreement with the expected values. This suggested a significant decrease in solubility of AgCl in the sample solution in the presence of ethanol. The use of a higher percentage of ethanol was preferred as it would also support the reduction of Cu^{2+} to Cu^+ (20). Chloride estimates based on the results of four samples (20 determinations) showed better precision for 5, 10, and 15% (v/v) ethanol samples as compared to the 20% (v/v) ethanol samples. Thus, further studies were carried out with the addition of 15% ethanol.

Effect of Other Halides on the Determination of Chloride

The Br^- and I^- ions, when present in the sample, would affect chloride estimation, whereas the presence of F^- ion would not interfere in the Cl^- determination as AgF since it is easily soluble in the sample solution. However, the interference of Br^- and I^- on the Cl^- determination could be overcome either by chemical separation of Br^- and I^- from the sample or by addition of a metal ion other than silver to the sample solution, resulting in insoluble precipitates of Br^- and I^- . Thus, the added silver is available for the selective precipitation with chloride to give AgCl. In this connection, Cu^{2+} , which exhibits interesting properties in going from Cu^{2+} to Cu^+ , can be tried as a possible masking agent for overcoming Br^- and I^- interference. The Cu^{2+} ion was reported (21) to stabilize as Cu^+ (cuprous) ion in the presence of solvents such as methanol, ethanol, 1-propanol, 2-propanol, pyridine, etc. Further, the cuprous salts of Br^- and I^- , i.e., CuBr and CuI , are reported to be insoluble, while those of Cl^- and F^- , i.e., CuCl_2 and CuF_2 , are soluble (20). This would keep total chloride in solution which can be precipitated as AgCl.

The effect of Br^- and I^- (1–25 $\mu\text{g/mL}$) on 0.25 to 25 $\mu\text{g/mL}$ of chlorine was investigated at varying concentrations of copper (0 to 50 $\mu\text{g/mL}$) added in the presence of ethanol [15 % (v/v)]. The results are shown in Table III. The chloride estimates had shown positive bias in the absence of copper addition (Table IIIA), whereas with copper addition in ethanolic uranium solution the chlorine estimates were in close agreement with the expected values. Further, the effect of varying amounts of Br^- and I^- and the copper addition on chlorine estimation (Table III, B and C) suggested that a copper addition up to 50 μg did not affect the chloride estimates. These studies suggested that the higher amounts of ethanol used in the present experiments helped in the reduction of Cu^{2+} to Cu^+ , which formed insoluble cuprous salts of Br^- and I^- , thereby removing the interference of these elements on chlorine. The presence of other halides, i.e., Br^- and I^- in the range 1–25 $\mu\text{g/mL}$, did not affect the chloride estimation in the range of 0.25–25 $\mu\text{g/mL}$ when copper up to 50 $\mu\text{g/mL}$ was added to the sample.

The results of the chloride determination in synthetic samples are listed in Table IV. Based on the analysis of 1 mL and 2.5 mL aliquots of chloride in the range of 0.5 to 25 $\mu\text{g/mL}$ (1–50 ppm), these levels can be determined in a uranium matrix in the presence of 25 $\mu\text{g/mL}$ of Br^- and I^- . The precision of the determinations, as calculated from the repetitive analyses of the synthetic samples, was found to be better than 15% RSD in the working range. The results of the chloride determination for real samples (taken in duplicate) and obtained with 1.0 and 2.5 mL aliquots are listed in Table V. Real samples were subjected to silver estimation prior to the chloride determination and the Ag concentration was found to be less than 0.1 ppm. The chloride values in the real samples showed

good agreement with the reported spectrophotometric values. The present method compares well with the spectrophotometric method. The GFAAS method developed in this study for chloride determination is free from any Br^- and I^- interference and does not involve prior separation of the major matrix.

CONCLUSION

A method was developed for the GFAAS determination of chloride in the presence of other halides (Br^- , I^- and F^-) without chemical separation of the uranium matrix using silver as a concentration probe. The copper in the ethanol medium was found to be an effective masking agent for overcoming the interference of the bromide/iodide ions. Using the optimized method, chloride can be determined in a uranium matrix in the range 0.5–50 ppm in the presence of 50 ppm each of bromide and iodide with a precision of 15%.

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