Determination of Cu and Mn in Uranium by Inductively Coupled Plasma Atomic Absorption Spectrometry (ICP-AAS)

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INTRODUCTION

Nuclear power has been produced in thermal reactors in many countries for more than five decades. Most of the thermal reactors in operation at present are of two types (a) light water reactors (BWR's = boiling water reactors and PWR's = pressurized water reactors) using low enriched uranium fuel and (b) heavy water reactors using natural uranium fuel. It was realized quite early that energy from uranium (U) can be extracted and with this in view, the quality control of U-based nuclear materials is essential. The quality control of U is also essential as uranium is used in Pressurized Heavy Water Reactors (PHWR), and U+Th is the proposed fuel for Advance Heavy Water Reactors (AHWR) (1). Chemical quality control (CQC) provides a means to ensure that the quality of the fabricated fuel conforms to the chemical specifications for the fuel laid down by the fuel designer. The specifications are worked out for the major and minor constituents which affect the fuel properties and hence its performance under conditions prevailing in an operating reactor. Each fuel batch has to be subjected to comprehensive chemical quality control for trace constituents, stoichiometry, and isotopic composition. The determination of impurities in uranium at various stages of the nuclear fuel cycle plays an important role in quality control and achievement of physical, chemical, and metallurgical requirements. It

ABSTRACT

A unique inductively coupled plasma atomic absorption spectrometry (ICP-AAS) system has been developed and was used for the determination of Cu and Mn at sub-nanogram levels in clean and complex solutions. Characteristic concentrations were obtained in the presence and absence of uranium. The sensitivity and linear range remained unchanged in the uranium matrix.

The analytes were determined in the concentration range of 0.1–1.0 ppm for Cu and 1.0–10 ppm for Mn, with a precision better than 1%. The amount determined in the present work using ICP-AAS provides lower determinations for these analytes than those reported earlier for other ICP-AAS units. This probably may be due to the fact that the presently designed ICP-AAS unit provides better discrimination against plasma background, reduction of aerosol absorbance with the incorporation of a desolvation unit, and simpler absorption measurements. In addition, the sensitivities obtained for these analytes in ICP-AAS were found to be better than that with GF-AAS. The enhancement in sensitivities for these analytes may be attributed to the increase in the number of atoms available in the ICP atomizer in the gaseous state at high temperature.

is, therefore, necessary to characterize U for trace metallic constituents as part of its chemical quality control (CQC). Also Mn-65 is one of the elements among various activated corrosion products, which is known to create radiation

field problems by γ -emitting activities.

A number of analytical protocols have been used for the elemental characterization of plutonium, uranium, and thorium matrices, and, depending upon the analytes required, the concentration range of impurities, required precision, sample throughput, and time of analysis. These various methods include inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), graphite furnace atomic absorption spectrometry (GF-AAS), and recently also high performance liquid chromatography ICP-MS (HPLC-ICP-MS). Of these, GF-AAS (2–4), ICP-AES (5, 6) and ICP-MS (7–8) are amenable to the routine elemental analysis at trace levels in a very wide range of sample matrices. However, the presence of a complex matrix severely affects the quantitative determination of individual elements, especially at trace levels in many of the ICP-based analytical techniques.

Inductively coupled plasma (ICP) was introduced as an efficient high temperature excitation source with minimal chemical interferences in analytical methods based on the atomic emission spectrometric (AES) technique (9–10). However, ICP-AES suffers from severe spectral interference in the presence of a matrix having a line-rich emission spectrum. Wendt and Fassel (11) reported for the first time the development of AAS with ICP as an atomizer. Subsequently, detailed ICP-AAS investigations (12) as an analytical technique were carried out which led to the conclu-

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sion that although ICP-AAS was feasible, it suffered from poor detection limits due to the high "background" emission of the energetic plasma. A recent publication (13) reported a unit free from these drawbacks and proved that ICP-AAS can be used for the direct determination of elements at ultra-trace concentrations in the presence of a uranium and thorium matrix. Due to the limited use of ICP-AAS systems in industry, these systems are typically not commercially introduced.

In the present work, atomic absorption spectrometric methods were developed using an ICP-AAS unit for the direct determination of Cu and Mn in uranium and thorium matrices. The ICP-AAS that has been developed (13,14) has an atomizer with modulated hollow

cathode lamps (HCL) and a synchronized elemental detection system along with the dispersing lens to reduce the background continuum arising from the plasma source.

EXPERIMENTAL

Instrumentation

Development and Design Features of the Present ICP-AAS System

While designing the ICP-AAS system, attention was focused on achieving a large optical path length, higher HCL emission throughput, and reduction in background associated with the atomizer. Based on these design aspects, an axial-viewed plasma unit with a 40.68 MHz operating r.f. frequency was procured from Jobin Yvon, France. Modulated HCLs and a syn-

chronized detection unit were procured from Chemito Technology Pvt. Ltd., India, for reducing atomizer background.

The procured units were appropriately modified before assembling them to form a single ICP-AAS system. In the assembled unit, a high spurious absorbance signal was observed and identified as being due to water aerosol in the light path. The spurious absorbance signal was reduced by controlling aerosol formation and its solvent content by incorporating a desolvation unit (procured from Scientific Apparatus Mfg. Co. India) immediately next to the nebulizer.

To facilitate passing of the HCL beam through the sample mist, the plasma torch assembly was modified. A T-shaped joint was incorporated with a 0.5 mm thick quartz window (see Figure 1). The HCL radiation thus obtained was allowed to pass through the center of the modified plasma torch assembly having a 2.8 mm aperture in the alumina injector. On incorporation of these changes, the fully assembled ICP-AAS system was used for the present studies.

Elemental and uranium matrix solutions were prepared as described by Goyal et al. (13). The schematic of the ICP-AAS instrument used is shown in Figure 2.

RESULTS AND DISCUSSION

There have only been three ICP-AAS reports published (12-14) for the determination of analytes in uranium and thorium matrices. Thus, this technique has the capability to be further developed. In this paper, the ICP-AAS system as previously described by Goyal et al. (13) is used for the determination of Cu and Mn. High purity quartz double distilled (QDD) water gave an absorbance of approximately 2.5 at the most sensitive line of Mn (279.48 nm), while for Cu at its

Fig. 1. Photograph of the instrument and ICP chamber with Heating ribbon for ICP-AAS unit.

Fig. 2. Schematic diagram of in-house designed ICP-AAS system.

most sensitive line (324.8 nm) no background absorbance was obtained with QDD water. As a result, the most sensitive line for Cu (324.8 nm) and a less sensitive spectral line (403.08 nm) for Mn were used. For Mn at its less sensitive line (403.08 nm), no background absorbance was obtained with QDD water. The relative sensitivity of the 403.08 nm spectral line is known to be 8% less than the 279.48 nm spectral line of Mn.

Studies were carried out to optimize the parameters for the HCL current, plasma power, heating rate of the aerosols, sample uptake rate/pump speed, and monochromator band width both in the absence and presence of the matrix (1 mg/mL U). The instrumental operating conditions are listed in Table I.

These parameters were used for establishing the analytical curves for Cu and Mn. Net absorbance signals were plotted and characteristic concentrations (CC=concentration corresponding to an

absorbance = 0.0044) were obtained. The analytes were determined in the concentration range of 0.0001–0.001 µg/mL for Cu and 0.001–0.01 µg/mL for Mn in pure nitrate solution with a precision better than 1% (listed in Table II).

In order to check for spectral, physical, or chemical interferences in a U matrix, the absorption measurements were carried out for Cu and Mn in the 1 mg/mL U matrix. The absorbance signals of both analytes remained unchanged in the U (1 mg/mL) matrix blank in comparison to the QDD water blank. These results show that there is no spectral interference while working in the AAS mode with ICP, unlike the AES mode (12). The analytes Cu and Mn were determined in the concentration range of 0.0001–0.001 and 0.001–0.01 µg/mL, respectively, in 1 mg/mL U. This corresponds to 0.1–1 ppm and 1–10 ppm for Cu and Mn, respectively, on the basis of 1 mg/mL U, with a precision better than 1%. Characteristic concentrations, sensitivity, and linear range remained

the same with and without 1 mg/mL of U matrix for both elements. These results convey that there is no interference of any type from the uranium matrix.

The analytical data obtained with the ICP-AAS unit were compared with those reported on such units earlier (12), with the conventional graphite atomizer (15,16) and with ICP-AES.

Comparison of Sensitivities by Present ICP-AAS to Reported Data (12)

Hensman et al. (12) attributed the difference in sensitivity for Cu in U in comparison to pure nitrate solutions mainly to the variations in background noise, which is indicative of a noise source dominated by the light source. However, the data obtained in this study did not show any change in sensitivity for both analytes (Table II). This could probably be due to the reduced background noise with use of the synchronized elemental detection system (SED) and modulated HCL source (13,14), which discriminates against the background. Although, an 8 times less sensitive line of Mn is used (403.08 nm) in the present work, as compared to an earlier work (279.48 nm) (12), it is interesting to note that the characteristic concentration is four-fold better than the reported work by Hensman et al. (12).

The much lower characteristic concentration obtained in the present work resulted from the incorporation of a desolvation unit to reduce absorbance by the aerosol. Due to a reduced blank absorbance signal, the analyte absorbance could be measured at a much lower concentration than the previously reported data (12).

TABLE I
Instrumental Operating Conditions for Cu and Mn

S. No.	Parameters	Optimized for Cu	Optimized for Mn
1	HCL current	10 mA	10 mA
2	Plasma power	1000 W	1000 W
3	Monochromator band width	0.5 nm	0.5 nm
4	Analytical line	324.8 nm	403.08 nm
5	Peristaltic pump speed	7 RPM	7 RPM
6	Desolvation temperature	200 °C	200 °C

TABLE II
Comparison of Characteristic Concentrations in U to the U-free Solutions

Present work (ng/mL)			Reported (12) (µg/mL)		
Element λ	Clean Solution	Complex Solution	Element λ	Clean Solution	Complex Solution
Cu 324.8 nm	0.006	0.006	Cu 324.8 nm	0.6	0.36
Mn 403.08 nm	0.039	0.041	Mn 279.5 nm	0.39	0.4

Comparison of Results for GF Atomizer With ICP Atomizer

In graphite atomizers (GF), carbon participates not only in the formation of the carbides of the elements (17), but also in the reduction of the oxides to free metal. In comparison to the GF atomizer, an ICP atomizer has an inert Ar environment and by virtue of its high temperature, the only mode of atomization in ICP is oxide dissociation. It was reported for Ag (18), Cd, Cu, and Mn (19) that in a GF atomizer when AgNO_3 , $\text{Cd(NO}_3)_2$, $\text{Cu(NO}_3)_2$, and $\text{Mn(NO}_3)_2$ are atomized, Cd and Mn undergo oxide dissociation, while Ag and Cu undergo a carbothermic reduction reaction. However, the sensitivities obtained for Cu and Mn presently are better with the ICP atomizer than with GF, and hence the mode of atomization alone does not explain the better sensitivities for Cu and Mn in the ICP atomizer. A comparison of lowest amount obtained using GF and ICP-AAS is given in Table III.

To understand the unusual behavior of these analytes, the physico chemical criteria, given in Table IV, are considered. The oxide dissociation energies and appearance temperature (T_{app}) required for Mn and Cu atomization are much higher than those required for Ag and Cd atomization. Appearance temperature (20) is the lowest temperature where a detectable signal was obtained above the blank signal.

The partial pressure of Ag, Cd, Cu, and Mn atoms in inductively coupled plasma and the graphite furnace atomizer were calculated based on the methodology reported by Belov et al. (22). The calculated percentage increase in partial pressure of Cu and Mn atoms in inductively coupled plasma (ICP mean temperature $\sim 5500^\circ\text{C}$) (23) is higher in comparison to graphite furnace (GF mean temperature $\sim 2500^\circ\text{C}$), while it is lower for Ag

and Cd in ICP as compared to that of the GF atomizer. The details are given in Table V.

The combined effects of physico chemical properties, increase in partial pressure of atoms at higher temperatures in the ICP atomizer (as compared to the GF atomizer), and the dilution effects associated with the ICP atomizer explain the trend in the sensitivities of Cu and $\text{Mn} > \text{Ag}$ and Cd in the ICP atomizer, compared to Ag and $\text{Cd} > \text{Cu}$ and Mn in the GF atomizer.

The sensitivity obtained is almost independent of matrix with the ICP atomizer, unlike its suppression in a GF atomizer for Cu

(15) and Mn (16). Thermogravimetric analysis of uranyl nitrate indicated (24) that its decomposition to dioxide takes place in the temperature range of $227\text{--}1227^\circ\text{C}$. As a result, UO_2 is formed, has a very stable lattice, and entraps the analytes. UO_2 dissociates only above 3000°C , which is not attainable in a GF atomizer, and the analytes remain trapped in the UO_2 lattice which results in poor atomization. Matrix-independent sensitivity in ICP-AAS can probably be attributed to the availability of high temperature where the lattice of uranium (uranium oxide) (7.7 eV) gets dissociated in the ICP (11.55 eV) (25) and the analytes are free for absorption measurements.

TABLE III
Comparison of Lowest Amount Obtained Using GF and ICP-AAS

Element	λ (nm)	AAS ICP ($\mu\text{g/mL}$)	GF ($\mu\text{g/mL}$)	Comparison of Sensitivities in ICP & GF-AAS
Cu	324.8	0.0001	0.005 (15)	ICP atomizer > GF atomizer
Mn	403.0	0.001	0.01 (16)	ICP atomizer > GF atomizer
Ag	328.1	0.01	0.002 (13)	GF atomizer > ICP atomizer
Cd	228.8	0.01	0.002 (13)	GF atomizer > ICP atomizer

TABLE IV
Melting and Boiling Temperatures for Elements and Their Oxides

Element	Oxide Energy (KJ/mole)	GF Atomizer T_{app} ($^\circ\text{C}$)	Oxide ($^\circ\text{C}$) (21) M.P.	B.P.	Element ($^\circ\text{C}$) (21) M.P.	B.P.
Ag	244	907	d 300	-	960	2212
Cd	340	447	d 900	subl. 1559	320.9	765
Cu	500	997	1235	-	1083	2595
Mn	650	1207	1705	-	1244	2097

d = Decompose.

subl. = Sublime.

TABLE V
Partial Pressure of Analyte Atoms in ICP, GF Atomizers,
and % Increase in ICP Atomizer

Element	Partial Pressures (in atm.) GF Atomizer	ICP Atomizer	% Increase of Partial Pressure of Atoms in ICP Atomizer $\times 10^2$
Cu	0.9082	742.4	817
Mn	0.00343	64.656	18850
Ag	9.366	1250.8	138.88
Cd	51.358	742.4	14.455

Table VI
Comparison of Sample Analysis Using ICP-AES and ICP-AAS

Element	ICP+AAS				ICP+AES (Radial)			
	Clean Solution ($\mu\text{g/mL}$)		U Complex Solution ($\mu\text{g/mL}$)		Clean Solution ($\mu\text{g/mL}$)		U Complex Solution ($\mu\text{g/mL}$)	
	Added	Obtained	Added	Obtained	Added	Obtained	Added	Obtained
Cu 324.8nm	0.000	0.000	0.000	0.000	0.0	0.0	0.0	0.33
	0.0005	0.0005	0.0005	0.0005	0.1	0.13	0.1	0.71
Mn 403.08 nm	0.0	0.0	0.0	0.0	0.0	0.0 (257.6nm)	0.0	0.08 (257.6nm)
	0.005	0.005	0.005	0.005	0.1	0.13 (257.6nm)	0.1	0.14 (257.6nm)

Fig. 3. Analytical curves (a) Mn (b) Cu in aqueous and U solutions..

Comparison of Results With Present ICP-AAS Studies to the ICP-AES Reported or From Lab Data

A challenge for any practical instrument is the ability to monitor accurately and precisely an analyte while discriminating against any matrix interference. Therefore, in order to check the spectral interference due to the U matrix with ICP-AAS, the absorption measurements were carried out for the analytes in the U matrix at the concentration of 1 mg/mL. The absorbance signal remained unchanged for 1 mg/mL U blank in comparison to the QDD water blank. These results show

that there is no spectral interference while working in the AAS mode with the ICP atomizer.

Similar experiments were carried out in the AES mode with the ICP atomizer. Table VI shows the concentrations determined and the corresponding blank using ICP-AAS with both clean and complex samples. The amount obtained at blank level for a complex sample (Cu and Mn - 0.0 $\mu\text{g/mL}$ and U - 1 mg/mL), and as demonstrated by the ICP-AAS configuration, are reasonable; but of more interest is that ICP-AES shows a concentration of 0.33 $\mu\text{g/mL}$ for Cu and 0.08 $\mu\text{g/mL}$ for Mn. A spectral interference is observed in

case of emission detection. This concludes that with ICP-AAS there is no difference in the signal for both Cu and Mn in a sample with and without matrix in contrast to the ICP-AES where the sample with matrix and sample without matrix shows different signals.

The limit of quantitative determination (LOQD) results with ICP-AAS are much better than with the ICP-AES. Even at the high temperatures, which exist in an ICP in the range of 1000-10,000 $^{\circ}\text{C}$, it has been calculated that most atomic species are present in their respective ground state rather than in the excited or ionic state. Therefore, it can be stated that the atomic absorption mode (AAS) has better sensitivity than the atomic emission mode (AES).

Analytical Results

The analytical curves of Mn and Cu in an aqueous and uranium matrix in the ICP-AAS mode are shown in Figure 3 (a and b), respectively. As seen from the figures, no degradation in sensitivity was observed in the uranium matrix as compared to the pure nitrate solutions. The Cu in the U matrix showed a parallel shift in comparison to the uranium matrix-free solution due to a contribution from the U blank.

TABLE VII
Characteristic Concentrations (C.C.) and Linear Analytical Range for Cu and Mn Determination

Sample		Cu			Mn		
		GF-AAS (15)	ICP-AAS Present work	Ref. (12)	GF-AAS (16)	ICP-AAS Present Work	Ref. (12)
Aqu.	C.C.x10 ⁺³ (µg/mL)	1.7	6.9x10 ⁻³	600	2.1	3.9 x10 ⁻³	390
	Range (µg/mL)	0.005-0.4	0.0001 - 0.001	-	0.01-0.2	0.001 - 0.01	-
U	C.C.x10 ⁺³	4.9	6.0x10 ⁻³	360	5.0	4.1	400
	Range (µg/mL)-	0.01-0.5	0.0001 - 0.001	-	0.02-0.6	0.001 - 0.01	-

Analytical data (such as characteristic concentration and analytical range) for these analytes were obtained. The results and those reported in the literature on similar ICP-AAS systems and with the reported GF-AAS data from our laboratory are given in Table VII. As seen from this table, these analytes were determined directly in the concentration range of 0.1–1 ppm and 1–10 ppm for Cu and Mn, respectively, in the presence of 1 mg/mL U. In contrast to the chemical separation procedure generally adopted with an ICP source in the AES mode (5-6), the present method ensures least handling of the sample and also minimal contamination in comparison to procedures requiring extensive use of chemical reagents during matrix separation. The characteristic concentrations and linear range of the analysis with and without 1 mg/mL U matrix remained the same for both elements.

The precision of determination was better than 1% and far superior to the GF-AAS based method, which is mainly due to the stability of the ICP source and the inert environment of the ICP atomizer. In the absence of a certified sample, the performance of the methods was evaluated by analyzing three synthetically prepared samples. The results obtained for these analytes are given in Table VIII and indicate close agreement with the added contents.

TABLE VIII
Analysis Results Obtained for Cu and Mn in Presence of U Matrix

Sample No.	Cu Concentration (ppm)		Mn Concentration (ppm)	
	Added	Obtained	Added	Obtained
1	0.2	0.2 ± 0.002	2	2 ± 0.02
2	0.5	0.5 ± 0.004	4	4 ± 0.03
3	0.8	0.8 ± 0.006	6	6 ± 0.05

CONCLUSION

In this work, accurate and precise methods were developed for the direct determination of Cu and Mn in nuclear-grade uranium oxide by inductively coupled plasma atomic absorption spectrometry (ICP-AAS). The presently designed ICP-AAS unit provides simple absorption measurements with improved sensitivity in the presence of uranium matrix without pre-treatment of the sample. The sensitivity and linear range remained unchanged with and without uranium matrix.

The analytes were determined in the concentration range of 0.0001–0.001 µg/mL for Cu and 0.001–0.01 µg/mL for Mn in the presence of 1 mg/mL uranium solution. The amount determined in the present work using ICP-AAS provides lower determination for these analytes than those reported earlier for such units.

ACKNOWLEDGMENT

The authors are grateful to Dr. Ashok Goswami, Head, Radiochemistry Division, for his keen interest and constant encouragement in the course of this work.

Received April 17, 2012.

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