

Rapid and interference free determination of ultra trace level of uranium in potable water originating from different geochemical environments by ICP-OES

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Abstract Direct determination of uranium in the concentration range of $8 \mu\text{g L}^{-1}$ to mg L^{-1} in water samples originating from different geochemical environments has been done using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Uranium detection with 2–3% RSD (relative standard deviation) has been achieved in water samples by optimizing the plasma power, argon and sheath gas flow. These parameters were optimized for three different emission lines of uranium at 385.958, 409.014 and 424.167 nm. Interference arising due to the variation in concentration of bicarbonate, sodium chloride, calcium chloride, Fe and dissolved organic carbon (DOC) on the determination of uranium in water samples was also checked as these are the elements which vary as per the prevailing geochemical environment in groundwater samples. The concentration of NaHCO_3 , CaCl_2 and NaCl in water was varied in the range 0.5–2.0%; whereas Fe ranged between 1 and $10 \mu\text{g mL}^{-1}$ and DOC between 0.1–1%. No marked interference in quantitative determination of uranium was observed due to elevated level of NaHCO_3 , CaCl_2 and NaCl and Fe and DOC in groundwater samples. Concentration of uranium was also determined by other techniques like adsorptive stripping voltametry (AdSv); laser fluorimetry and alpha spectrometry. Results indicate

distinct advantage for uranium determination by ICP-OES compare to other techniques.

Keywords Uranium · Potable water · ICP-OES · Interference · Geochemical environment

Introduction

Uranium is present in the earth's crust, principally in the hexavalent form and its contamination in ground water is a matter of great concern because of its high toxicity as a dissolved heavy metal. Nephrotoxicity is the primary chemically induced effect of uranium in human beings, while it is also considered as carcinogenic, causing bone cancer. Uranium is detected in groundwater in several areas across the world specially in areas where the rock structure is dominated by uranium bearing minerals. The recommended maximum admissible concentration (MAC) of uranium in drinking water decided by the World Health Organisation (WHO) is currently $15 \mu\text{g L}^{-1}$ [1]. Therefore, direct determination of the low level concentration of uranium in ground water has been taken up by various radio-analytical groups around the world. Different techniques were in practice for the rapid and interference free determination of uranium in water samples. Major Techniques like Alpha Spectrometry, Adsorptive Stripping Voltametry (AdSv), Laser Fluorimetry have some or other limitations. Alpha spectrometry need a very thin electroplated sources and long counting time although free from elemental interference [2]. Adsorptive stripping voltametry (AdSv) and laser fluorimetry are very sensitive techniques but prone to many interferences. Dissolved organic carbon (DOC) and Cl^{-1} ions have marked interference in case of AdSv whereas bicarbonates and PO_4^{3-} have marked

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interference in case of laser fluorimetry [3, 4]. In order to carry out a quick determination with minimum interference, the determination of uranium was done using inductively coupled plasma optical emission spectrometry (ICP-OES) without any chemical pre-treatment.

Uranium in groundwater is present mainly due to the dissolution of soluble minerals and leaching due to rock-water interactions. Main source of groundwater is in general due to the water entering the ground through precipitation. In principle it has essentially the same chemical composition as in the precipitation. However, as the water moves through the vadose zone its chemical composition changes due to the addition of organic material and soluble salts. In the saturated zone, the water is isolated from the atmosphere and as the water moves in the ground water, oxygen is consumed by the oxidation of DOC. This changes the oxidation–reduction potential of the system and leads to a variety of rock-water interactions. The origin of major aqueous species in ground water is given in Table 1 [5, 6].

In this work spectral interference from other metal ions was very effectively eliminated by selective selection of emission lines. The present investigation reports the determination of uranium in water samples by ICP-OES without having pretreatment. In addition to this the effect

of variation in concentration of NaHCO_3 , CaCl_2 and NaCl in uranium determination was also studied.

Materials and method

Sample collection

The ground water samples were collected from six different locations spread over a distance of 4 km at Trombay, Mumbai having latitude $19^\circ 00' 498$ (N) and longitude $72^\circ 55' 136$. Triplicate samples were collected in one liter pre-acid washed polypropylene bottles. Various physico-chemical characteristics including the concentration of uranium was measured in these samples.

Reagents and test solutions

Reagents of highest purity grade were used: 65% HNO_3 (Suprapure, Merck) and deionized water from Millipore RiOs™. The stock solution of uranium was prepared from uranyl nitrate (Aldrich catalogue No 207624) having a concentration of $973 \mu\text{g mL}^{-1}$ in 1% HNO_3 . The experimental solutions were prepared, by spiking the collected sample with the stock solution of uranium after filtration through $0.45 \mu\text{m}$ filter using suction filtration. The samples were stored for 4 weeks to develop equilibration under N_2 atmosphere. The various physicochemical characteristics of the samples were measured before and after spiking the samples with uranium.

Sample preparation and optimum operation conditions for uranium determination by ICP-OES system

Groundwater samples were filtered using suction filtration and filter membrane having pore size of $0.45 \mu\text{m}$. Filtered water samples were directly nebulized by using Meinhard concentric glass nebulizer into the plasma at flow rate of 0.9 mL min^{-1} . Simultaneous solid state detector inductively coupled plasma optical emission spectrometer (ICP-OES, model ACTIVA S, from Horiba Jobin–Yvon SAS, France) was used. ACTIVA utilizes a 2048×512 pixel, ultra-low noise, advanced inverted mode operation (AIMO), back illuminated (BI), high quantum efficiency charge coupled device (CCD) solid-state detector. ACTIVA includes a unique optical design featuring a 0.64 m Czerny–Turner optical system and holographic gratings of 4343 grooves per mm and 2400 grooves per mm. covering the full 6 mm height of the plasma normal analytical zone multi-WAV acquisition mode provides complete sample fingerprinting of 75 elements in less than

Table 1 Origin of major aqueous species in groundwater [5]

Aqueous species	Origin
Na^+	NaCl dissolution (some pollution) Plagioclase weathering Rainwater addition
K^+	Biotite weathering K-feldspar weathering
Mg^{+2}	Amphibole and pyroxene weathering Biotite (and chlorite) weathering Dolomite weathering Olivine weathering Rainwater addition
Ca^{+2}	Calcite weathering Plagioclase weathering Dolomite weathering
HCO_3^-	Calcite and dolomite weathering Silicate weathering
SO_4^{2-}	Pyrite weathering (some pollution) CaSO_4 dissolution Rainwater addition
Cl^-	NaCl dissolution (some pollution) Rainwater addition
$\text{H}_4\text{SiO}_{4(\text{aq})}$	Silicate weathering

Table 2 Specification of HORIBA Jobin–Yvon ACTIVA S (France) ICP-OES system and operating conditions for the measurement of uranium

Monochromator	HORIBA Jobin–Yvon ACTIVA S
Mounting	Czerny–Turner, focal length 0.64 m
Grating and wavelength range	Holographic, 4343 grooves mm ⁻¹ (from 160 to 430 nm, first order)
Spectral resolution	Less than 20 pm between 190 and 430 nm
Detectors	2048 × 512 pixel, charge coupled device (CCD)
Rf generator	Solid state with water cooling
Frequency	40.68 MHz
Power output	0.7–1.0 kW
Observation	Radial
Nebulizer	Meinhard, concentric glass
Spray chamber	JY Glass cyclonic spray chamber
Plasma torch	Fully demountable torch
Injector tube diameter of torch	3 mm
Pump	Peristaltic, three channels, twelve-roller
Operating conditions	
Outer argon flow rate (L min ⁻¹)	12
Sheath gas flow rate (L min ⁻¹)	0.4
Liquid uptake rate (mL min ⁻¹)	0.9
Nebulizer pressure (bar)	1
Nitrogen flow rate	$\lambda < 200$ nm, $\lambda < 400$ and $\lambda > 400$ optics was purged by 6, 4 and 0.5 L/min
Incident power (kW)	1

30 s. It gives resolution up to 20 pm. The details of various other optimized parameters are given in Table 2.

Sample preparation for uranium determination by alpha spectrometry

3 mL filtered sample was transferred to a beaker and dried on a hot plate after which it was dissolved in 1.2 mL of 0.1 N H₂SO₄ mixed with 10 mL of electrolyte solution of (NH₄)₂SO₄ having pH 3.2. The pH of the resultant solution was 2.2. The solution was electroplated as discussed above and counted for 240,000 s. Details of the same are discussed elsewhere [2].

Sample preparation for uranium determination by Laser fluorimeter

A pulsed nitrogen laser of 337.1 nm wavelength was used to excite Uranyl species. The luminescence and life time

measurements were made using the sealed nitrogen laser. Details of the same are discussed elsewhere [4].

Results and discussion

The detection capability and resistance to chemical interferences of any measurement process is an important performance characteristics of a technique for the accurate determination of element either at trace level or at ultra trace level. In general the composition of the matrix, influences its quantitative determination, therefore it is of utmost importance to study the composition of the matrix.

Variation in the groundwater compositions

Table 1 give the origin of the major species present in the groundwater. From the table its clear that the predominance of one process over the other varies its composition. Oxidation and reduction (Redox) reactions play an important role in the geochemical processes that occur in groundwater. Groundwater typically contains both reduced and oxidized species, however, what is termed the redox buffer capacity of an aquifer is normally dominated by the chemistry of the aquifer matrix most natural. In groundwater systems iron is the dominant buffering species involved in redox reactions [6]. In some organic rich aquifers DOC can equal ferrous iron as a reduction buffer. The concentration of iron and DOC along with other physicochemical characteristics of the water sample is given in the Table 3. In case of spiked samples, the concentration of sodium, calcium and bicarbonate varies in the range 0.5–2.0%. The concentration of Fe and DOC varies between 1–10 $\mu\text{g mL}^{-1}$ and 0.1–1%. The variation of these caused a marked impact on the redox potential of the groundwater samples.

Table 3 Mean value of various physicochemical characteristics of the ground water before and after spiking

Parameters	Un-spiked	Spiked
pH	7.7–8.1	7.4–8.2
E.C. μS	350–450	360–500
Redox potential (mV)	150–250	40–400
HCO ₃ ⁻ (mg L ⁻¹)	180–190	180–2.0%
Na ⁺ (mg L ⁻¹)	28–40	27–2.0%
K ⁺ (mg L ⁻¹)	0.75–1.2	0.72–1.4
Ca ²⁺ (mg L ⁻¹)	39.26–50	37.26–2.0%
Fe ³⁺ (mg L ⁻¹)	0.2–0.4	0.2–10
DOC (ng L ⁻¹)	20–30	30–1.0%
Uranium (ng L ⁻¹)	ND (<2)	10–11

Direct determination of uranium in groundwater sample using optimized parameters of ICP-OES:

Calibration parameters of three different emission line of uranium

In pure solvent (de-mineralized water) spiked with uranium standard solution the calibration parameters were evaluated using all the three emission lines of uranium (385.958, 409.014 and 424.167 nm). The different values of the evaluated parameters is shown in Fig. 1. From the figure it is clear that the lines at 385.958, 409.014 nm are the most sensitive one as background equivalent concentration (BEC) is 0.863 and 0.71 ng mL⁻¹ respectively, however, BEC at 424.167 is 56.9 ng mL⁻¹. Therefore, during the present work the average concentration obtained at emission lines 385.958 and 409.014 nm is only considered. The detection limit of the method is 3*SD₀, where SD₀ is the value of the standard deviation as the concentration of

the uranium in the sample blank. The value of SD₀ was obtained in all the blank sample separately having different concentration of sodium chloride, calcium chloride, sodium bicarbonate, Fe and DOC. Since slight differences in the matrix could cause a considerable systematic error having a definite bias therefore internal standardization has been adopted to evaluate the matrix element impact.

Accuracy of analytical results

Accuracy or Bias can be best established through the analysis of a certified reference material (CRM, or SRM if obtained from NIST). During this work, in-house standard reference of groundwater samples was prepared having a concentration of 20 µg L⁻¹. The results of uranium concentration from ICP-OES were in good agreement with the certified value of SRM (In house) within ±5% experimental error. A precision of better than 0.20% at the 95% uncertainty level ($n = 5$) has been obtained.

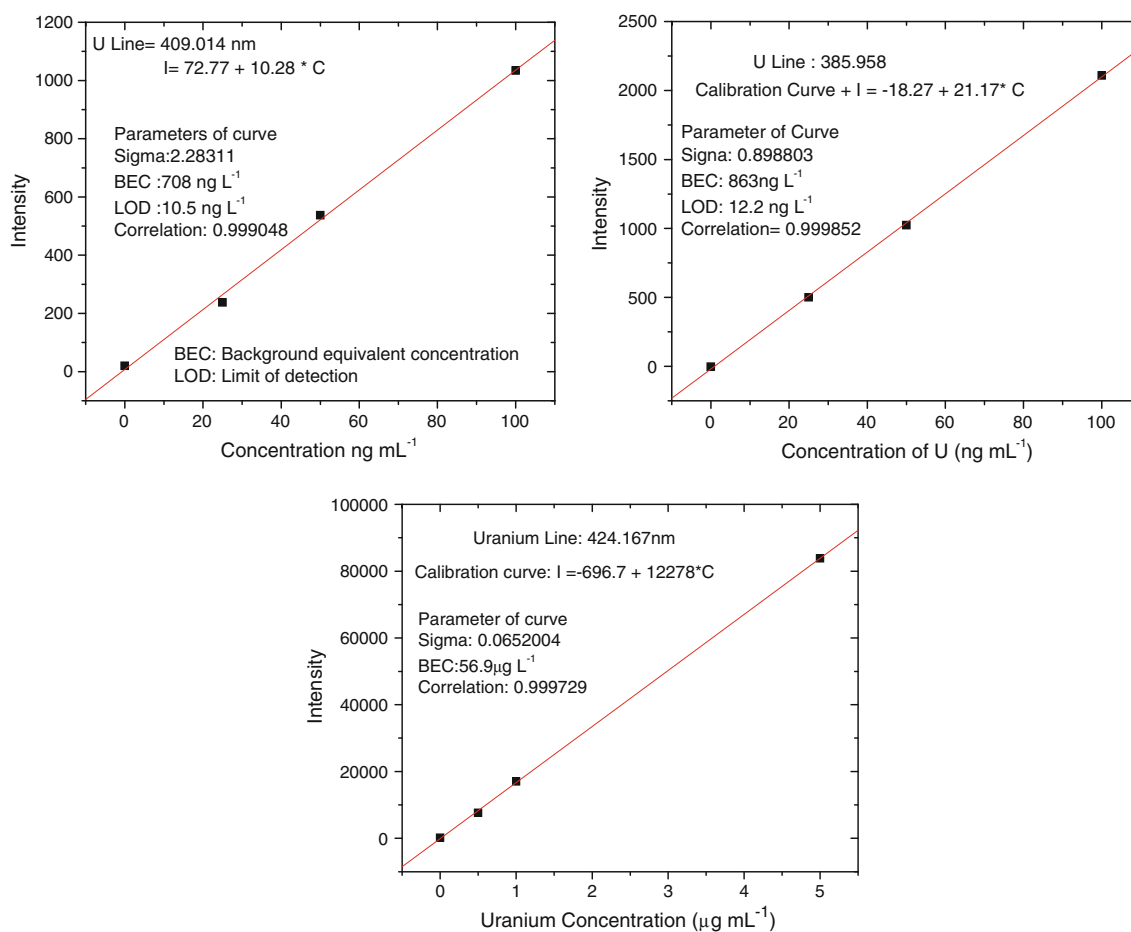


Fig. 1 Calibration graph at three different emission line in case of standard sample prepared by spiking de-mineralized water with standard solution of uranium

Uranium measurement in groundwater samples having different compositions

Figure 2 shows the recovery of uranium in groundwater samples under normal conditions (groundwater, does not contain elevated level of any elements/compound). From this figure it is clear that recoveries are more than 98% in the concentration range of 10–25 $\mu\text{g mL}^{-1}$. Figures 3, 4, 5, 6 and 7 give the uranium concentration in different water sample having varying degree of Ca^{2+} , HCO_3^- , Na^+ , DOC (dissolved organic carbon) and Fe^{3+} . In these samples concentration of HCO_3^- , Ca^{2+} and Na^+ varies from 0.5 to 2.0% and the concentration of Fe and DOC varies in the range of 1–10 $\mu\text{g mL}^{-1}$ and 0.1–1% respectively. From these figures it is evident that the determination of uranium by ICP-OES does not get interference due to either of the above. As observed from the Fig. 3, an increase in concentration of uranium is observed with the increase in the concentration of bicarbonate. This increase is due to the uranium content associated with sodium carbonate solution (90 ng mL^{-1} in case of solution of 1%) which is used to spike the sample for carbonate.

Comparatives determination of uranium by three different techniques

In order to compare the results obtained from ICP-OES with other probable techniques, solution having 2% of either sodium bicarbonate or calcium chloride or sodium chloride or 1% DOC or 10 $\mu\text{g mL}^{-1}$ Fe, having uranium concentration 10 ng L^{-1} was analyzed by four different techniques (Alpha spectrometry, Laser Fluorimetry, AdSV and ICP-OES). In case of alpha spectrometry direct electroplating was done and the same sample was analyzed

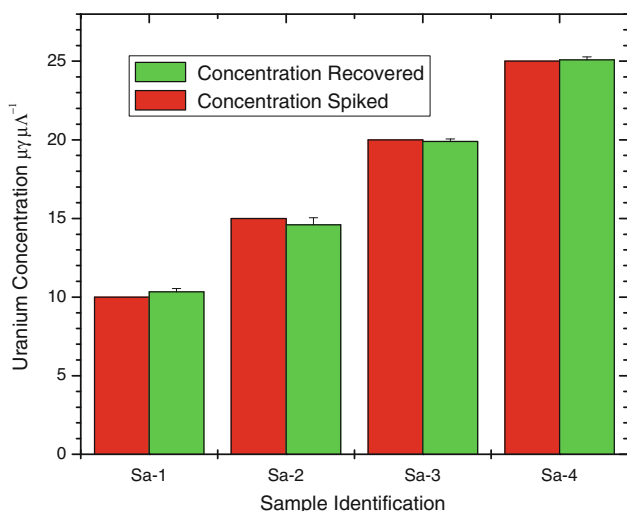


Fig. 2 Determination of uranium in groundwater samples under normal conditions

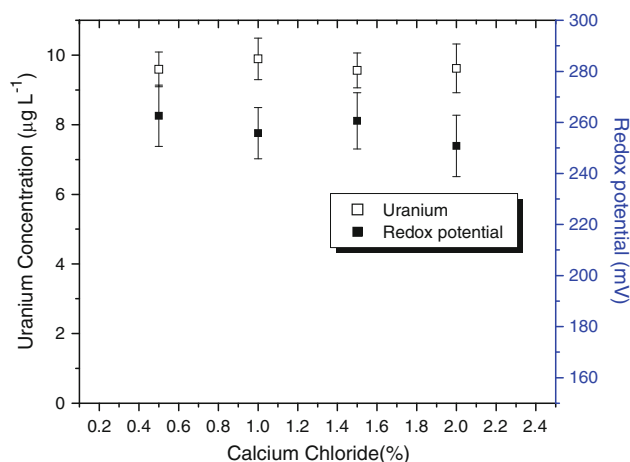


Fig. 3 Variation in uranium concentration and redox potential in groundwater sample at different levels of CaCl_2

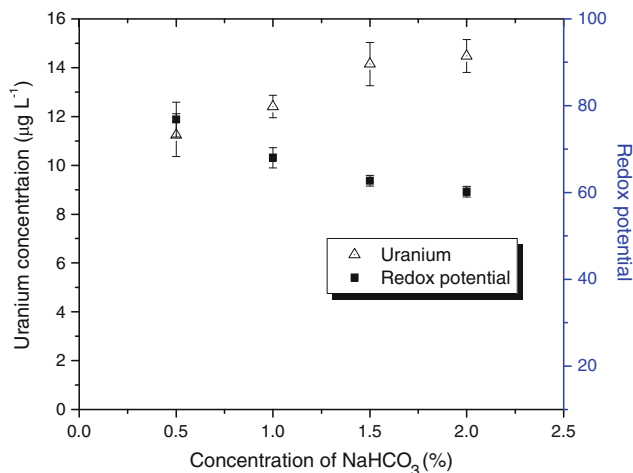


Fig. 4 Variation in uranium concentration and redox potential in groundwater sample at different levels of sodium bicarbonate

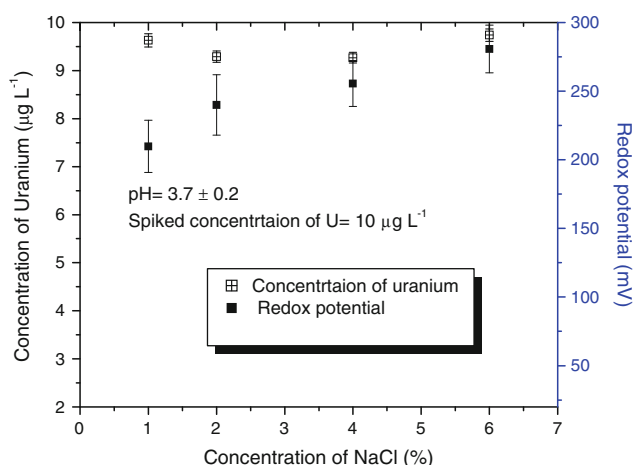


Fig. 5 Variation in uranium concentration and redox potential in groundwater sample at different levels of sodium chloride

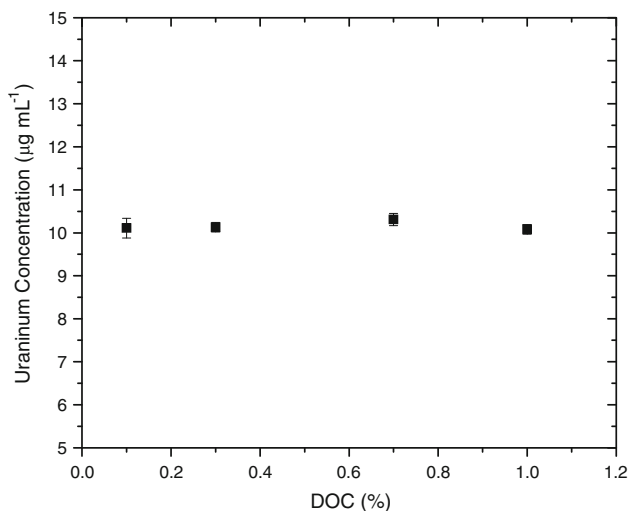


Fig. 6 Variation in uranium concentration and redox potential in groundwater sample at different levels of dissolved organic carbon (DOC)

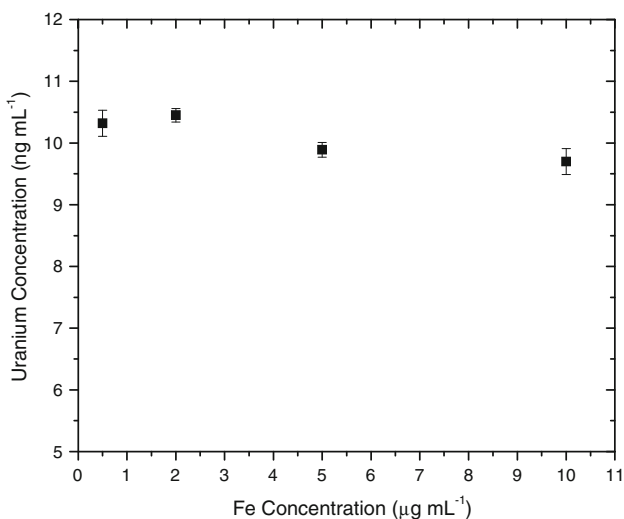


Fig. 7 Variation in uranium concentration and redox potential in groundwater sample at different levels of Fe

using adsorptive stripping voltammetry by forming uranium chloranilic acid complex (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone), details of the same were discussed elsewhere [3–7]. The analysis of sample was also performed by scavenging uranium either with calcium as $\text{Ca}_3(\text{PO}_4)_2$ or Fe as mixed hydroxide of $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_2$ and counting by alpha spectrometry. The results of all the four techniques are given in Table 4. From this table it is clear that alpha spectrometry and ICP-OES are the best techniques for groundwater as they have minimum interference. In case of alpha spectrometry, the biggest disadvantage is its time consuming and needs special efforts for sample preparation. As alpha radiations are short range radiation the sample must be electroplated either on stainless steel or platinum before counting by alpha spectrometry. As is evident from the Table 4, there is about 40% suppression in uranium concentration in case of determination by alpha in presence of Fe. As Fe also gets electrodeposited along with U resulting in thick coating [8–10]. The fact is verified by separating the Fe from U by using anion exchange column and thereby electrodepositing the samples where 100% recovery was observed. The details of the procedure are discussed elsewhere [8]. Similar observation were made by the work carried by Dampare et al. [11] and Guogang et al. [12] where uranium determination was done by instrumental neutron activation analysis (INAA) and alpha spectrometry respectively. Their work clearly indicate the number of interferences and large time required for the analysis. Another major advantage of uranium determination by ICP-OES is that the technique is free from speciation as the uranium is converted to elemental uranium in the plasma. The emission lines from the elemental uranium is used for the quantitative measurement. As discussed by Chopin, the environmental chemistry of uranium is largely dictated by its formal oxidation state [13, 14]. Under ambient oxidizing conditions, the predominant uranium oxidation state is U(VI). Where

Table 4 Comparative determination of uranium by various technique in water samples having different compositions

Techniques →	Laser fluorimetry	Alpha spectrometry	ICP-OES	Adsorptive stripping voltammetry
Quality →	(Rapid)	(Tedious and time consuming)	(Rapid)	(Rapid)
Groundwater sample having 2% NaCl	10.23	10.23	10.23	ND (Interference due to Cl^{-1})
Groundwater samples having 2% HCO_3^{-1}	ND (interference due to HCO_3^{-1})	11.42	11.02	10.31
Groundwater samples having 2% CaCl_2	ND (Interference due to Ca^{2+}) due to formation of Calcium Phosphate	10.32	10.13	ND
Groundwater sample with 1% Dissolved Organic Compound	ND (interference from DOC)	10.13	10.11	ND
Ground water sample having Fe $10 \mu\text{g mL}^{-1}$	10.12	6.78	10.13	10.12

oxygen is limited, U(IV) may dominate. The metallic form, U(0), does not occur naturally, and is readily oxidized to U(IV), and eventually U(VI), upon exposure to oxidizing conditions.

Conclusions

Compared to other techniques like alpha spectrometry, laser fluorimetry, adsorptive stripping voltametry, ICP-OES is a versatile technique for the determination of uranium since the emission lines caused by the presence Na^+ , Ca^{2+} and Fe will be resolved efficiently because of very high spectral resolution (<20 pm) detector. In addition to this due to the high temperature of plasma, interferences from DOC and HCO_3^- is not possible as they get converted into volatile species as soon as they enter into the analytical zone.

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