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# Analysis of iron-rich hydrochloric acid solutions for uranium, thorium, rare-earth elements and other heavy metals

Beena Sunilkumar<sup>1\*</sup> , M. Krishnakumar<sup>2</sup> and A. A. Patwardhan<sup>1</sup>

## Abstract

A simple solvent extraction method is described for the separation of trace elements including uranium (U), thorium (Th) and rare-earth elements (REEs) from industrially processed iron-rich hydrochloric acid solutions. Iron (Fe) causes severe spectral interference during the analysis of trace elements using inductively coupled plasma optical emission spectrometer (ICP-OES) and U by light-emitting diode (LED)-based fluorimeter (LEDF). The spectral interferences of Fe on trace elements are studied and documented. Sequential solvent extractions using methyl isobutyl ketone (MIBK) effectively removed the highly interfering Fe from these processed acid solutions, thereby enabling accurate and sensitive determination of Cd, Zn, Pb, Co, Ni, Cr, V, Cu, Sr, Zr, Ti, REEs including radioactive elements like U and Th. Solvent extraction parameters like the number of extractions, aqueous-organic ratio and acidity have been optimized for removal of Fe. The accuracy of the method has been established by analyzing synthetically prepared hydrochloric acid solutions by spiking-recovery method. Ion exchange separation of REEs using Dowex 50 × 8 cation exchange resin has been also studied and reported. The precision obtained has been well within ± 10% RSD for elements having concentration above 10 mg L<sup>-1</sup> and ± 15% for elements having concentration below 10 mg L<sup>-1</sup> for replicate (*n* = 5) measurements.

## Introduction

Hydrochloric acid (HCl) is a strong inorganic acid with a large number of industrial applications. It is extremely corrosive and its aggressiveness can change drastically depending on its concentration, temperature and presence of oxidizing impurities (Mishra et al. 2016). It is mainly used as a solvent for the extraction of metals from its ores like ilmenite, bauxite, etc. (Artem Sokolov et al. 2021). One of the most commonly found matrix elements in most ores is iron (Fe). Titanium pigment industries use HCl or chlorine to remove major matrix element

such as Fe from ilmenite (Chun Li et al. 2008; Wahyungsih et al. 2014; Lavasani et al. 2019). The reactivity of Fe in ilmenite ore during leaching with hydrochloric acid is greatly enhanced when it is present in ferrous, Fe(II) state. The reduction of Fe in ilmenite is mainly carried out by heating the ore with coke in an inert atmosphere. After reduction, Fe is leached with HCl and the leached iron finds application in making strong bricks used for construction works. Waste and tailings from iron ore mining plants are utilized for the manufacture of construction materials (Sreekant et al. 2016). The ores and coke used for reduction of Fe contain heavy metals. The acid-leached iron liquid contains many toxic and radioactive elements, which can cause environmental effects. The leaching of heavy metals from bricks are determined by their solubility. Toxic characteristic leaching procedures of bricks have been done to assess the environmental compactability of clays, sludges, mine wastes,

\*Correspondence:

Beena Sunilkumar  
beena.amd@gov.in

<sup>1</sup> Department of Atomic Energy, Atomic Minerals Directorate for Exploration and Research (AMD), Begumpet, Hyderabad 500016, India

<sup>2</sup> Department of Atomic Energy, Atomic Minerals Directorate for Exploration and Research (AMD), Nagarbhavi, Bengaluru 560072, India



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etc., from construction materials like bricks and cements (Wiebusch et al. 1998; Valls and Vazquez 2002; Weng et al. 2003; Fang-Chih et al. 2007; Cusido and Cremades 2012). An attempt has been made to analyze the heavy metals, radioactive elements and economically important metals in the raw material of processed HCl solutions prior to manufacturing bricks considering the economic and environmental impacts.

Inductively coupled plasma optical emission spectrometry (ICP-OES) is widely utilized as an efficient technique for trace level determination of trace elements including REEs and Th. Emission line rich elements like Fe in the matrix causes severe spectral interferences in the determination of elements using ICP-OES. Therefore, analysis of trace elements in processed hydrochloric acid solutions from ilmenite industry is all the more challenging owing to the very high amounts of iron ( $>20 \text{ g L}^{-1}$ ) present in such samples. The direct analysis of these processed hydrochloric acid solutions is difficult due to the high acidity and viscosity arising from the high Fe content. The analysis of trace impurities in such samples is necessary for the quality control of the recovered HCl and also the by-products generated. Many separation techniques like solvent extraction (Stafilov and Zendelovska 2002; Pradhan and Ambade 2021), co-precipitation, selective precipitation (Matsumiya et al. 2013), ion exchange (Walsh et al. 1981; Jarvis 1988), chromatography and sorption (Murty et al. 2002; Adarsh Kumar et al. 2007) have been reported for determination of REEs and other trace elements in iron-rich minerals and steel materials. Extraction chromatography was used for the separation of REE in Fe-rich water samples (Gonzalez et al. 2005). Instrumental techniques like Inductively coupled plasma Mass spectrometer (ICP-MS) and Radiochemical neutron activation analysis (RNAA) were also used for the analysis of trace elements in Fe-rich materials (Balaram et al. 1992; Balaram 1996; Makreski et al. 2008).

Liyi Zhou et al. used neutral extractant like methyl isobutyl ketone (MIBK) for separation of Fe from geological samples to remove the iron interference for geochemical analysis of Fe-rich geological samples by atomic absorption spectrometry (AAS) (Liyi Zhou et al. 1985). Mixed solvent systems like tri-butyl phosphate (TBP)-MIBK were used for the separation of Fe from titania wastes (Reddy and Sarma 1996; Saji and Reddy 2001) and di-2-ethyl hexyl phosphoric acid (D2EHPA)-MIBK for extraction and stripping of Fe from concentrated acid chloride solutions (Sahu and Das 2000). Cation and anion exchange chromatographic separation methods are also in use for trace level separation and preconcentration of REEs in geological samples (Crock and Lichte 1982, 1986; Satyanarayana 2007).

The spectral interference of Fe on REEs, U and Th in Fe containing minerals has been extensively studied and reported. MIBK is used as an organic solvent for the separation of Fe from geological samples for the determination of REEs by ICP-OES in certified reference materials like SY-2, SY-3 obtained from CCRMP, Canada which contain 6.3 and 6.5% (by weight) of total  $\text{Fe}_2\text{O}_3$  (Khorge et al. 2000). However, studies related to trace elemental determination in industrially processed liquids are elusive, which is important from economical as well as environmental perspective. However, the actual recoveries of heavy elements like U and Th in the aqueous phase or organic phase in the extraction procedure have not been reported so far.

In the present work, MIBK has been employed for the extractive separation of Fe (III) prior to the determination of trace elements, REEs and radioactive elements like U and Th by ICP-OES. The recoveries of elements have been verified using spiked synthetic samples. The optimized parameters for extraction has been applied for the determination of trace constituents in highly acidic processed iron-rich (Fe-rich spent and recovered HCl) solutions, which are by-products of titanium dioxide pigment industries.

## Experimental

### Reagents and standards

All reagents, hydrochloric acid (HCl), nitric acid ( $\text{HNO}_3$ ), o-phosphoric acid, methyl isobutyl ketone (MIBK) and ammonium dihydrogen phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) used were of analytical grade or better. The Fe solution was prepared from specpure Fe metal powder in 10% (v/v) HCl. All solutions were prepared in ultrapure (Type-I) water of conductivity  $\sim 0.05 \mu\text{S/cm}$ . Traceable elemental standard stock solutions ( $1 \text{ mg mL}^{-1}$ ) were procured from Inorganic Ventures, USA, and in-house standard solutions were prepared using specpure chemicals. Appropriate dilutions were carried out for preparing working calibration standards ( $0.1$  to  $10 \mu\text{g mL}^{-1}$ ). The purity of argon used in ICP-OES is 99.999%.

### Preparation of fluorescent enhancing buffer for uranium measurement by LED fluorimeter

Five hundred grams of ammonium dihydrogen phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) was weighed and dissolved in 1.5 L Type-I water. 120 mL of o-phosphoric acid was added to this and made up the volume to 2.0 L with Type-1 water with solution pH is 2.6 (Rathore et al. 2001). This solution acts as fluorescence enhancing reagent for the determination of uranium by LED fluorimeter.

### Instrumentation

**LED fluorimeter:** All the fluorescence measurements were taken with a microcontroller-based filter Fluorimeter. This is equipped with a pulsed light-emitting diode (6 LEDs in a ring) as excitation source which gives 20  $\mu\text{J}$  or higher energy per pulse. Fluorescence from uranyl species (514 nm) is measured using a photo multiplier tube (PMT) attached to a precision multiplier and filter. Fluorescence measurements are possible through a dynamic range of 0.1–500  $\mu\text{g L}^{-1}$  of U. The fluorescence is detected by a pulsed photomultiplier tube (Pulse rate 1 kHz). Suitable filters after the LEDs and before the photomultiplier tube prevent LED light from reaching the photomultiplier tube directly. A single board computer averages the photomultiplier output over 2000 pulses and carries out any calculations necessary. The LED fluorimeter instrument (Model LF-2) used for the analysis is manufactured by Quantalase Enterprises Private Limited, Indore, India. This instrument is compact and is also operable on a 12 V battery source and consumes 8W power.

ICP-OES (Model: Ultima-2, Horiba Jobin Yvon, France) for determination of other elements. The optimum parameters and specifications of ICP-OES and LED fluorimeter are given in Tables 1 and 2, respectively. The atomic absorption spectrometer (AAS) (Model: novAA

300 by Analytik Jena, Germany) has been also used for comparison of results obtained with ICP-OES wherever possible.

### Procedure

#### Method-I: proposed method of removal of Fe using solvent extraction using MIBK

Ten milliliters of aliquots of test samples of spent HCl and recovered HCl solutions of 25–30% (v/v) acidity with respect to HCl were taken in a clean glass beaker and dried on a boiling water bath. To this 2 mL of concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  was added to oxidize the Fe completely and the solution was allowed to evaporate. Nitric acid treatment was repeated twice. Finally, the solution was prepared in 5 mL of 6 M HCl and extracted with 5 mL MIBK in a separating funnel. The contents were agitated for two minutes with frequent removal of volatile gases formed inside the separating funnel. Subsequently, the separating funnel was left standing for about two minutes for the complete separation of two layers. The aqueous layer and organic layer were separately collected in beakers. The extraction process was repeated using 5 mL MIBK each time, till the yellow color of the aqueous solution disappeared. The organic layer was collected each time in the same beaker. Finally, the organic

**Table 1** ICP-OES operating parameters

Parameter	Setting	Parameter	Setting
Mounting	Czerny–Turner	Frequency of generator	40.68 MHz
Focal length	1 m	Power	1000 W
Grating	4320 & 2400 grooves $\text{mm}^{-1}$	Plasma gas flow rate	12 L $\text{min}^{-1}$
Order of measurement	1st	Nebulizer gas flow rate	0.8 L $\text{min}^{-1}$
1st order resolution	0.005 nm	Nebulizer type	Meinhard
Type of generator	Solid state	Type of spray chamber	Cyclonic
Observation	Radial View	Injector tube diameter	1.8 mm

**Table 2** Operating parameters of LED Fluorimeter

Parameter	Setting
Power	8 Watts and operates on 12 V DC
Excitation Source	LEDs (light-emitting diodes), 405 nm
Detector	Photomultiplier tube
Analyte volume	Minimum 6 mL
Cuvette	External Size – 12.5 mm $\times$ 22.5 mm $\times$ 45 mm made from Ultra low fluorescence Fused Silica
Minimum Concentration	0.1 $\mu\text{g}$ uranium per liter
Dynamic range	0.1–1000 ppb
Accuracy	10% or 0.05 ppb whichever is larger
Reproducibility	Better than 5% under identical conditions at the time of measurement
Mode of operation	Uncalibrated Fluorescence Mode and instrument averages the fluorescence for 256 pulses and displays the average about 1 s for average of 256 pulses taken five times

layer was scrubbed with 5 mL of 6 M HCl to ensure the complete recovery of entrapped analytes into the aqueous layer from the organic layer. The aqueous layer was evaporated to dryness on a water bath and treated twice with 2–3 mL of concentrated HNO<sub>3</sub>. The aqueous layer was finally made up to 100 mL maintaining 3% (v/v) acidity with respect to HNO<sub>3</sub>. The solution was analyzed for trace elements and REEs by ICP-OES maintaining the working parameters as mentioned in Table 1.

#### Analysis of uranium by LED fluorimeter

An appropriate aliquot of Fe separated sample solution was taken in a 25-mL volumetric flask, and 10 mL of fluorescent enhancing buffer was added to the flask and made up to the volume using type-1 water. The calibration standards (1 ng mL<sup>-1</sup> to 100 ng mL<sup>-1</sup>) were also prepared in the same way by adding 10 mL fluorescent enhancing buffer. The fluorescence intensities were measured using LED fluorimeter. (Parameters are given in Table 2.)

#### Methods adopted for comparison

##### Direct measurement with matrix matched standards

A 10 mL aliquot of the sample was taken in a clean glass beaker and dried on a boiling water bath and nitric acid treatment was carried out as outlined in method-I. The final solution was made up to 100 mL maintaining 3% acidity with respect to HNO<sub>3</sub>. Two sets of trace elemental working calibration standards were prepared by maintaining 13 mg mL<sup>-1</sup> and 2.8 mg mL<sup>-1</sup> of Fe for matching to the samples and the absorbances were measured by AAS. The trace elements like Cu, Zn, Pb, Co and Ni were determined by AAS using two different sets of matrix matched calibration standards of 0.5 to 2 mg L<sup>-1</sup> range. The elements like Ca, Mg and Mn were determined using matrix matched calibration standards of 1, 2 and 5 mg L<sup>-1</sup> and Al using 5, 10 and 20 mg L<sup>-1</sup> standard concentrations, respectively.

##### Separation of REEs by cation exchange

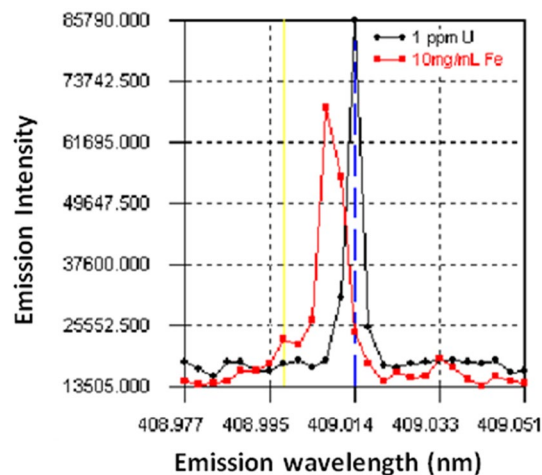
A 10 mL aliquot of the sample was taken in a clean glass beaker and dried on a boiling water bath. The residue obtained was treated with HNO<sub>3</sub> as outlined in method-I. The final solution was prepared in 1 M HCl. It was passed through the column filled (20 cm, 1 cm dia) with cation exchange resin, Dowex-50×8. After loading the column with sample solution it was washed with 100 mL of 1 M HCl to remove iron completely. Then the column was eluted consecutively with 75 mL of 6 M HNO<sub>3</sub> and 75 mL of 8 M HNO<sub>3</sub>. The flow rate of 1 mL min<sup>-1</sup> maintained for sample loading, washing and elution. The eluent loaded with analytes was collected, evaporated on a water bath, dried and made up to 25 mL maintaining an acidity of 3% (v/v) HNO<sub>3</sub>.

## Results and discussion

### Spectral interference of Fe

Spectral interferences caused by major matrix elements while determining trace concomitant elements is the major challenge during the ICP-OES analysis. Therefore, the interference of Fe on the determination of U, Th, Zr, Cd, V, Zn, Pb, Co, Ni, Cr and REEs by ICP-OES has been quantified. The emission line profiles of U, Th, Zn, Pb, Co and Cr clearly indicate a significant reduction in emission intensity in presence of high concentration of Fe. The spectral interference of Fe is very serious on Th 283.730 nm and Th 274.716 nm emission lines. Th 401.913 nm is relatively free from major element interference and is selected for analysis (Beena Sunilkumar et al. 2007). The U 409.014 nm line is selected for U determination, which is relatively free from the interference of Fe, still there is a wing overlap of Fe on U and given in Fig. 1. The reduction in the emission signal of 2 µg mL<sup>-1</sup> of uranium at 401.913 nm is observed above 300 µg mL<sup>-1</sup> Fe. When uranium is below 1 µg mL<sup>-1</sup>, the measurement is taken in a separated sample portion by LED fluorimeter. The fluorescence of U gets reduced by many elements, especially Fe (Krishnakumar et al. 2023), which is a strong quencher and the quenching behavior of Fe on uranium fluorescence is given in Fig. 2. U needs to be essentially separated from Fe before LED fluorimetric analysis.

The determination of low concentration of REEs in samples with high Fe content suffers from both spectral overlap interferences and matrix interferences. Spectral interferences can arise from direct line overlap, wing overlap or from the elevated background of REE emission peak caused by high Fe concentration. Direct line overlap interferences from Fe were observed on Tb (350.917 nm), Ho (345.600 nm), Yb (328.937 nm) and Lu (261.542 nm) (Figs. 3, 4, 5, 6). The Gd emission line



**Fig. 1** Interference of Fe on U emission line in ICP-OES

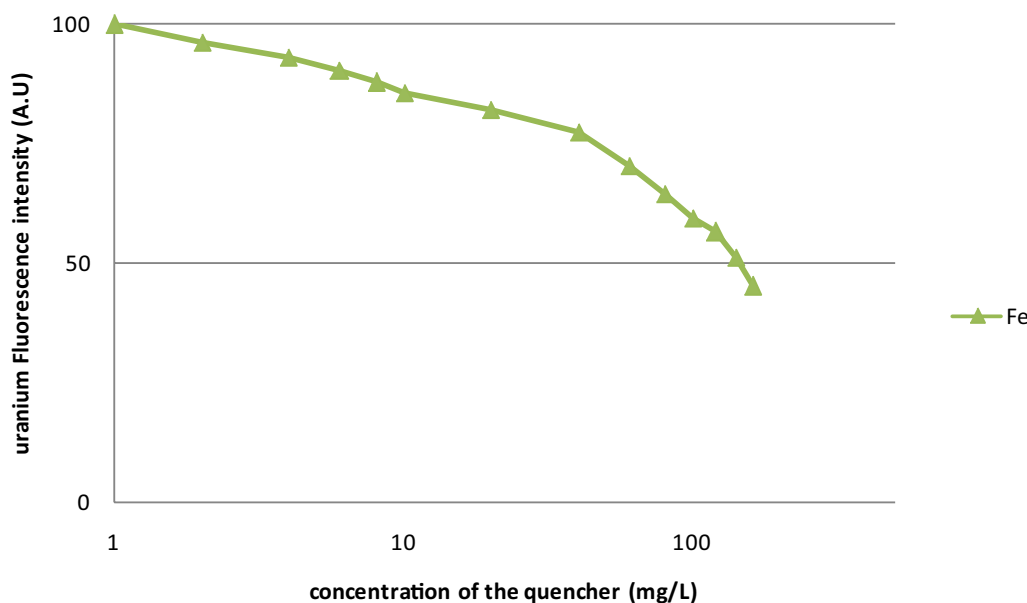


Fig. 2 Quenching of Fe on U (20 ppb) during LED Fluorimetric measurements

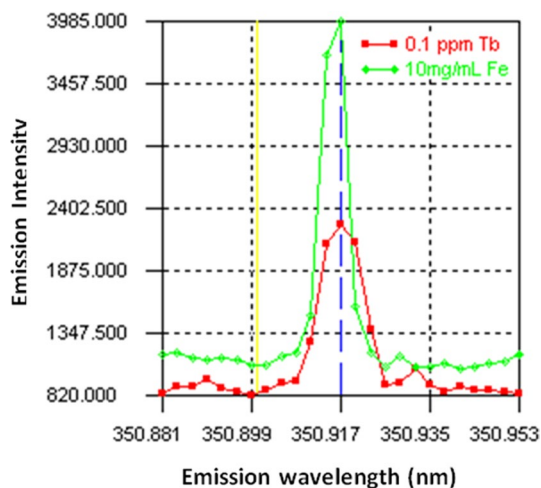


Fig. 3 Interference of Fe on Tb emission line, ICP-OES

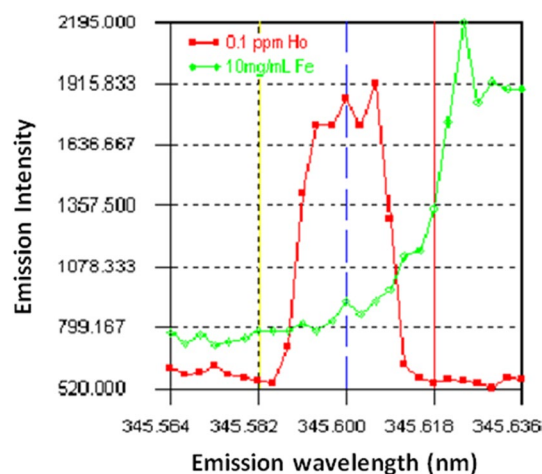


Fig. 4 Interference of Fe on Ho emission line, ICP-OES

at 342.246 nm, which has a serious wing overlap from Fe is omitted and the measurement was carried out 364.620 nm. In the case of Dy (353.170 nm), the high Fe concentration leads to elevated background intensity and hence resulted in erroneous result (Fig. 7). The matrix interference causes reduction in the transport efficiency of the nebulizer due to the high viscosity of the solution having high Fe content and also acidity. The high acidity of sample solution results in corrosion of nebulizer and spray chamber and also increases the memory effect in the subsequent measurements.

Similarly, emission line profiles of Cr, Co, Zn and Pb were also monitored in the presence of Fe (10 mg mL<sup>-1</sup>). It was found that the emission intensity of Cr (267.716 nm), Co (228.616 nm) and Zn (213.856 nm) gets depressed in the presence of Fe and a left side wing overlap is found on Pb (220.353 nm) (Figs. 8, 9, 10, 11).

It is observed that the dilution of the sample reduces the interference from Fe. However, dilution of sample degrades the determination limits and the analyses of all elements need to be carried out with matrix matched standards. Some elements like Zn, Pb, Co, Ni and Cr could not be determined accurately even with matrix matched standards due to the severe interference due to



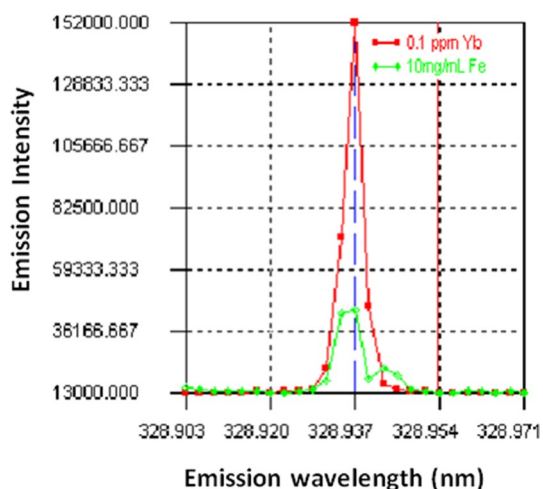


Fig. 5 Interference of Fe on Yb emission line, ICP-OES

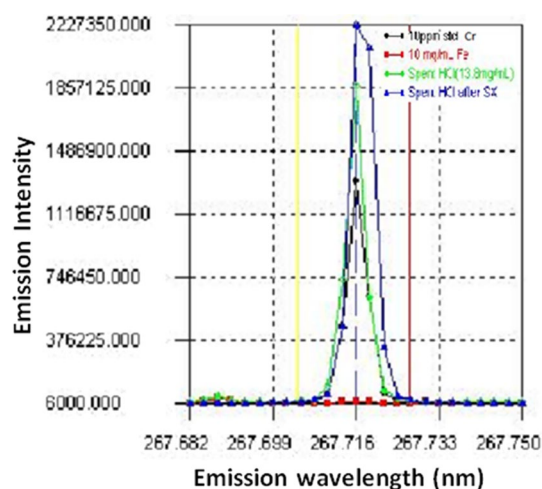


Fig. 8 Interference of Fe on Cr emission line, ICP-OES

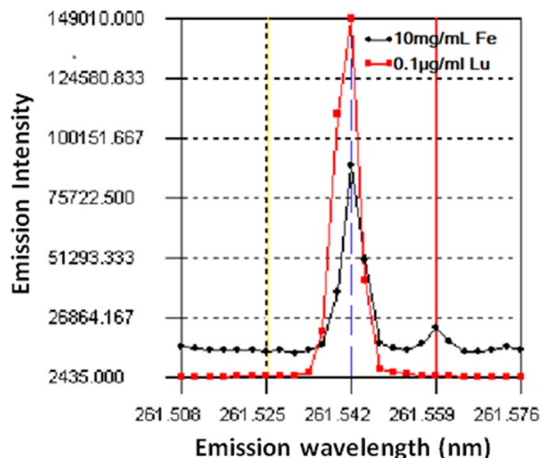


Fig. 6 Interference of Fe on Lu emission line, ICP-OES

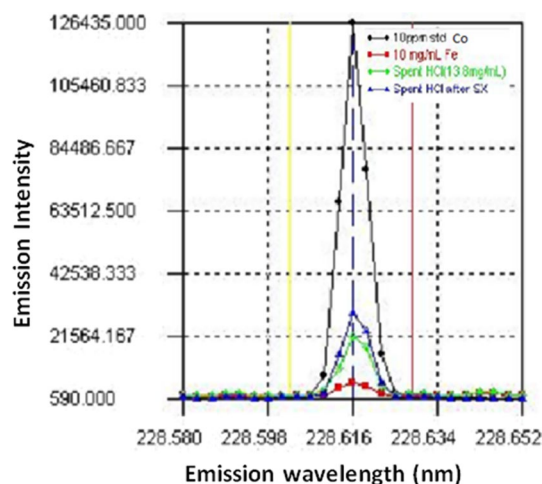


Fig. 9 Interference of Fe on Co emission line, ICP-OES

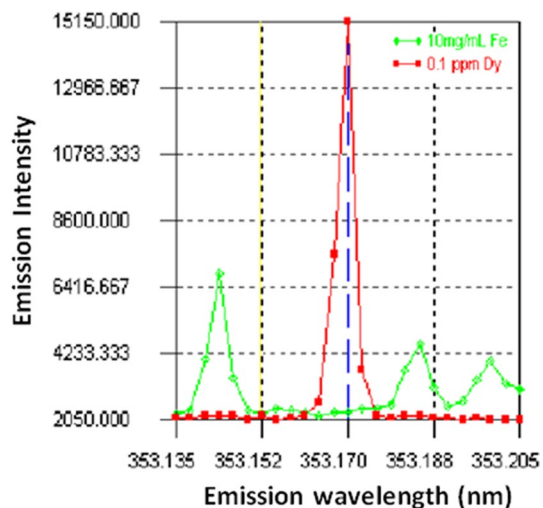


Fig. 7 Interference of Fe on Dy emission line, ICP-OES

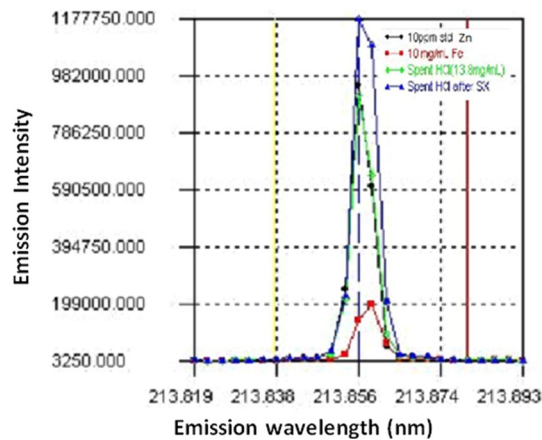
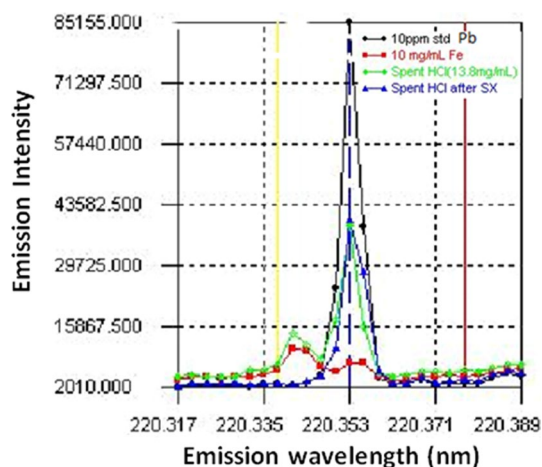


Fig. 10 Interference of Fe on Zn emission line, ICP-OES

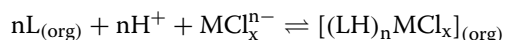


**Fig. 11** Interference of Fe on Pb emission line, ICP-OES

high Fe content. It is not convenient to match the matrix for all the samples due to the difference in Fe content in industrially processed liquids. Hence, the most effective alternate for accurate analysis of the trace constituents is the separation and removal of Fe using solvent extraction.

#### Solvent extraction with MIBK and optimization of number of extractions

MIBK ( $\text{CH}_3\text{COCH}_2\text{CH}(\text{CH}_3)_2$ ) is a well-known aliphatic ketonic solvent for extraction of Fe (III) from high acidic chloride solutions. Therefore, in this study also it was chosen as the solvent for extraction of Fe from highly acidic HCl samples containing high amounts of Fe. It is already known that, chloridometallates ( $\text{MCl}_x^{n-}$ ) of elements are present in aqueous solution at high chloride concentrations. The concentration of 6 M HCl was maintained for extraction of Fe. The Fe (III) chlorido complexes form outersphere assemblies or ion pairs with cationic extractants, which are responsible for their extraction into solvent. The  $\text{H}^+$  ion concentration present in the acid protonates the oxygen present in the extractant, the protonated extractant is responsible for the formation of outersphere complexes or ion pairs with the organic solvent. (Mathew Wilson et al. 2013)



In the above equation, 'M' represents metal ion, 'L' represents ligand, 'n' is the number of ligands participating in the reaction and 'x' is the number of chlorine atoms. Fe(III) in the form of  $\text{HFeCl}_4$  species may be responsible for its extraction to MIBK in the chloride medium (Reddy et al. 1996). Liyi Zhou et al. studied the extraction of Fe in the presence of ascorbic acid and reported that ascorbic acid prevents the extraction of Fe to MIBK. It may be due to the non-formation of either  $\text{HFeCl}_4$  or  $\text{FeCl}_4^-$  (Dodson

et al. 1936; Liyi Zhou et al. 1985). So the samples have been treated with oxidizing agents like  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  for oxidation of Fe(II) into Fe(III) prior to the extraction for complete removal of Fe, whereas, a minimum of 6 M acidity is required to keep the  $138 \text{ g L}^{-1}$  of Fe in solution.

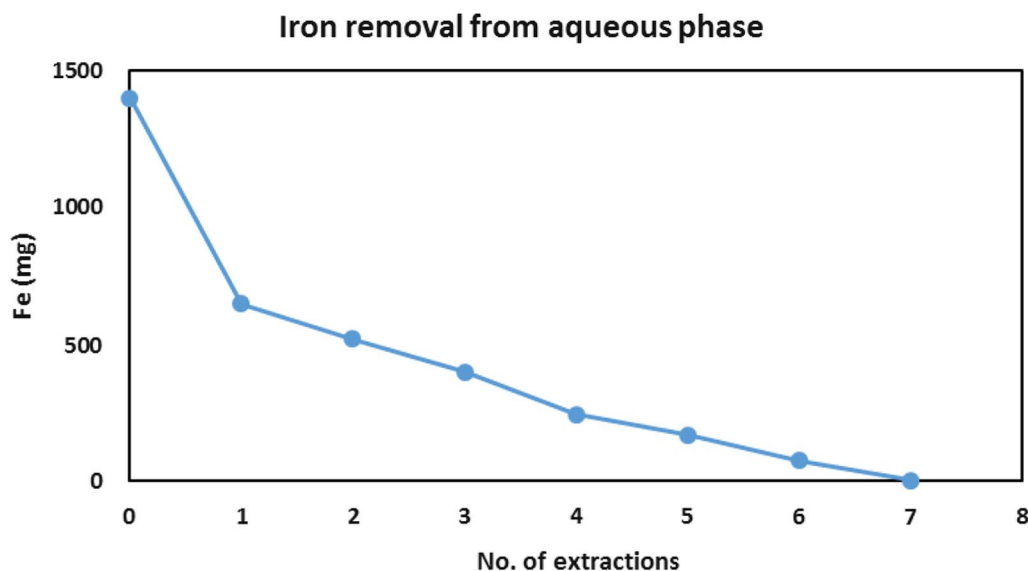
Synthetic samples were prepared by spiking the mixture of all analyte elemental standard solutions with Fe and subsequent drying on the water bath and finally dissolving in 5 mL of 6 M HCl. The samples were extracted with 5 mL MIBK and it is found that the number of extractions required for complete removal of Fe (III) depends on the Fe content of the solution. 10 mL of an industrial HCl sample solution containing  $138 \text{ g L}^{-1}$  Fe was extracted with MIBK and it was found that after seven extractions the Fe content in the aqueous layer reduced to  $< 100 \mu\text{g mL}^{-1}$ . The recovered HCl containing  $23 \text{ g L}^{-1}$  Fe, required only two extractions to remove the iron content and single extraction is sufficient for  $10 \text{ mg L}^{-1}$  Fe solution. The removal of Fe at different extraction stages for  $138 \text{ g L}^{-1}$  is given in Fig. 12.

#### Cation exchange chromatographic separation

Ion exchange chromatographic separation method using cation exchange resin, Dowex-50 $\times$ 8, was also attempted for separation of REEs from the Fe matrix. Initially, the column length was kept at 10 cm using 10 g resin for separation of Fe matrix. However, it has been found that column material is insufficient for holding the matrix completely. Hence, a 20-cm column was set up using 20 g resin and the experiments were repeated. This was sufficient, and the recovery of some of REEs in elute fraction has been found to be more than 90% in the case of recovered HCl containing  $23 \text{ g L}^{-1}$  Fe. Spent HCl had more Fe concentration of  $138 \text{ g L}^{-1}$ , and hence, the recovery of REEs has been found to be less quantitative when complete removal of Fe is not possible by cation exchange column chromatography.

#### Validation of the method

The validity of the method and the recovery of individual elements were studied by spiking with specpure elemental standards in HCl-Fe matrix solution. Quantitative recoveries were obtained for most of the elements using the suggested procedure. The recoveries for Zn, Mn, Ti, Pb, Co, Ni, Cr, V, Cu, Sr, Zr, Cd, Mg, Al, Ca, U, Th and REEs are quantitative in the range of 93.5% to 104%. However, for barium (Ba), the recovery was only 60% and molybdenum (Mo) was found to be co-extracted with Fe into MIBK. Mo forms an anionic chloride complex and behaves like ferric iron during the extraction process. The lower recovery of Ba may be due to the formation of chloridometallates at higher HCl concentration. The recovery studies were carried out using spiked



**Fig. 12** Removal of Fe with number of extractions

synthetic samples and the results are given in Tables 3 and 4. The residual Fe in the aqueous layer was reduced to  $80 \mu\text{g mL}^{-1}$  in the final solution after separation from the initial level of  $138 \text{ g L}^{-1}$  after seven sequential extractions with 5 mL each MIBK portions. Atomic Absorption Spectrometer (AAS) was also used for the validation of analytical data, wherever possible. Stafilov et al. reported

that in the presence of Fe, the absorbance of Co, Cr and Pb decreased and the absorbance of Ni increased (Stafilov and Zendelovska 2002). Determinations of Al, Ca, Mg, Mn, Cu, Zn, Co and Ni were carried out by AAS in dilute solutions after nitric acid and hydrogen peroxide treatment due to the presence of trace solvent organic matter in the processed solutions. Calibration of AAS

**Table 3** Analytical recovery of trace elements in synthetic mixtures [ $n = 3$ ]

Element	Wavelength (nm)	Element added ( $\mu\text{g}$ )	Element Recovered ( $\mu\text{g}$ )	Recovery (%)
Fe	259.940	1,000,000	80	<0.01
Mg	279.553	500	503	100.6
Al	309.284	500	499	99.8
Ca	422.673	500	494	98.8
Mn	257.610	500	500	100.0
Ti	334.941	500	505	101.0
Cd	226.502	500	477	95.4
Zn	213.856	200	206	103.0
Pb	220.353	200	187	93.5
Co	228.616	200	195	97.5
Ni	231.604	200	195	97.5
Cr	267.716	200	208	104.0
V	292.402	200	199	99.5
Cu	324.754	200	197	98.5
Sr	407.771	200	194	97.0
Zr	343.823	200	194	97.0
Th	401.913	200	187	93.5
U	409.014	200	192	96.0
Ba	233.527	200	120	60.0
Mo	202.030	200	5.0	2.5



**Table 4** Analytical recovery of rare-earth elements in synthetic mixtures [ $n = 3$ ]

Element	Wavelength (nm)	Element added ( $\mu\text{g}$ )	Element Recovered ( $\mu\text{g}$ )	Recovery (%)
Fe	259.940	1,000,000	80	<0.01
La	333.749	100	93.4	93.4
Ce	418.660	100	94.8	94.8
Pr	422.293	100	96.1	96.1
Nd	430.357	100	96.4	96.4
Sm	359.262	100	94.6	94.6
Eu	381.965	100	92.5	92.5
Gd	364.620	100	95.0	95.0
Tb	350.917	100	94.5	94.5
Dy	353.170	100	94.2	94.2
Ho	345.600	100	93.4	93.4
Er	349.910	100	92.8	92.8
Tm	346.221	100	94.5	94.5
Yb	328.937	100	94.4	94.4
Lu	261.542	100	94.5	94.5
Y	371.029	100	94.4	94.4

was carried out using matrix matched standards, otherwise, the analytical values obtained were lower when calibrated with pure standards. Matrix matching of standards is very important in these types of samples. Other elements could not be determined by AAS due to the very low concentration of analytes or interference due to the Fe matrix. The samples were directly analyzed by ICP-OES after calibrating the instrument with matrix matched standards and the concentration of Zn, Pb, Co, Ni, Cr and Sr were found to be on the lower side. The analytical data obtained by the proposed method of ICP-OES and the direct analysis with matrix matched standards by AAS for trace elements like Cu, Zn, Pb, Co and Ni are in good agreement, and the comparison of data is given in Table 5.

The accuracy of the results for REEs by the proposed method was verified by spiking studies. The recovery of REEs was found to be 92.5 to 96.4% (Table 4), and the RSD was found to be well within  $\pm 10\%$ . The recovery of all REE elements was not possible by ion-exchange separation method in these types of Fe-rich industrial liquids (Table 6).

The uranium content in the samples was lower than  $1 \mu\text{g mL}^{-1}$ , and it was difficult to be determined by ICP-OES. Therefore, the analysis of uranium was carried out by the sensitive LED fluorimetric technique after separation, and it was confirmed by spiking studies.

#### Application to samples

The method was applied to two industrial spent and recovered HCl sample solutions containing  $138 \text{ g L}^{-1}$  and  $23 \text{ g L}^{-1}$  Fe, respectively. The values of U, Th, trace

elements and REEs are given in Tables 5 and 6. The values were verified by direct measurements of dilute solutions by ICP-OES and AAS with matrix matched standards wherever possible. The number of extractions depends on the original Fe content of the solution, and the Fe concentration was reduced to  $< 100 \mu\text{g mL}^{-1}$  after seven sequential extractions for the spent HCl solution ( $138 \text{ g L}^{-1}$  Fe) and two extractions reduced the Fe in the recovered HCl ( $23 \text{ g L}^{-1}$  Fe) to  $< 100 \mu\text{g mL}^{-1}$ . It is also observed that dilution of the sample reduces the interference from Fe, but REEs, U and some trace elements could not be determined in the diluted sample due to the low concentration and spectral interference caused by Fe. In addition, dilution of sample degrades the determination limits and analysis of these trace elements needs to be carried out with matrix matched standards. It is not convenient to match the matrix for all the samples due to the large variation in Fe content of the samples. The values obtained by ICP-OES were compared well with those obtained by flame AAS for Cu, Zn, Co, Ni and Pb. The very low content of U was determined by LED fluorimeter, and it was verified by spiking studies. If necessary, the sample can be pre-concentrated after extraction for further improvement in the limit of determination.

#### Conclusion

The method of solvent extractive removal of Fe using MIBK has been applied to industrially processed HCl solutions with very high concentrations of Fe wherein co-extraction of analytes to MIBK is minimal except Mo. The cation exchange resin studied could not hold high Fe content in the studied liquids. Special longer

**Table 5** Analytical data of trace constituents in spent HCl (138 g/L Fe) and recovered HCl (23 g/L)

Element	Unit	Spent HCl containing 138 g L <sup>-1</sup> Fe			Recovered HCl containing 23 g L <sup>-1</sup> Fe		
		Solvent extraction using MIBK (n = 5)		Matrix matched calibration (n = 5)	Solvent extraction using MIBK (n = 5)		Matrix matched calibration (n = 5)
		ICP-OES		ICP-OES	AAS	ICP-OES	
Mn	g L <sup>-1</sup>	1.67	1.73	1.60	0.23	0.24	0.21
Mg	g L <sup>-1</sup>	2.60	2.35	2.55	0.37	0.36	0.34
Al	g L <sup>-1</sup>	1.50	1.48	1.55	0.23	0.22	0.25
Ti	mg L <sup>-1</sup>	32	25	–	7	7	–
Ca	mg L <sup>-1</sup>	355	350	360	78	80	70
V	mg L <sup>-1</sup>	310	300	–	47	46	–
Cu	mg L <sup>-1</sup>	9	10	10	1.6	1.7	2
Zr	mg L <sup>-1</sup>	< 1	< 1	–	< 1	< 1	–
Th	mg L <sup>-1</sup>	38	40	–	6	7	–
Zn	mg L <sup>-1</sup>	128	86	137	21	23	25
Pb	mg L <sup>-1</sup>	48	30	51	6	6	8
Co	mg L <sup>-1</sup>	25	18	23	4	4	3
Ni	mg L <sup>-1</sup>	15	10	17	2.5	2	2
Cr	mg L <sup>-1</sup>	185	130	–	28	29	–
Sr	mg L <sup>-1</sup>	25	22	–	3	3	–
U*	mg L <sup>-1</sup>	0.68	–	–	0.33	–	–

\* U was determined by LED Fluorimeter

–Below detection limits of ICP-OES

columns of high capacity resins are needed to separate REEs from this type of industrial liquids. Removal of Fe matrix improved the signal-to-noise ratio and in turn sensitivity in ICP-OES. Determination limit can be

**Table 6** Analytical data of trace REEs in spent HCl (138 g L<sup>-1</sup> Fe) and recovered HCl (23 g L<sup>-1</sup>)

Element	Unit	Spent HCl containing 138 g L <sup>-1</sup> Fe		Recovered HCl containing 23 g L <sup>-1</sup> Fe	
		SX (n = 5)	IE (n = 5)	SX (n = 5)	IE (n = 5)
La	mg L <sup>-1</sup>	70.0	50.0	13.0	14.0
Ce	mg L <sup>-1</sup>	122.0	94.0	22.0	20.0
Pr	mg L <sup>-1</sup>	14.8	11.0	2.5	2.1
Nd	mg L <sup>-1</sup>	58.0	45.0	10.2	8.4
Sm	mg L <sup>-1</sup>	9.0	7.0	1.7	1.4
Eu	mg L <sup>-1</sup>	0.58	0.52	0.11	0.10
Gd	mg L <sup>-1</sup>	4.20	3.80	0.69	0.61
Tb	mg L <sup>-1</sup>	0.37	0.50	0.07	0.07
Dy	mg L <sup>-1</sup>	1.70	1.50	0.28	0.23
Ho	mg L <sup>-1</sup>	0.36	0.28	0.06	0.04
Er	mg L <sup>-1</sup>	0.70	0.60	0.10	0.10
Tm	mg L <sup>-1</sup>	0.10	0.07	0.02	0.01
Yb	mg L <sup>-1</sup>	1.00	0.50	0.17	0.06
Lu	mg L <sup>-1</sup>	0.11	0.08	0.02	0.05
Y	mg L <sup>-1</sup>	4.70	4.20	0.79	0.65

SX Proposed method of solvent extraction using MIBK

IE Ion-exchange separation

improved by taking more sample volume for separation. The analytical recovery obtained varied from 92.5% (in the case of Eu) to 104% (in the case of Cr). The RSD is within  $\pm 10\%$  by ICP-OES measurements of elements having concentration above 10 mg L<sup>-1</sup> and  $\pm 15\%$  for elements having concentration below 10 mg L<sup>-1</sup> for five replicate measurements. The suggested method of MIBK extraction is very reliable for the accurate determination of uranium, thorium and all rare-earth elements in industrially processed acidic solutions. This method can also be applied for the determination of trace elements in Fe-rich geological materials like hematite, magnetite, ilmenite, etc.

**Abbreviations**

REEs	Rare-earth elements
ICP-OES	Inductively coupled plasma optical emission spectrometry
AAS	Atomic absorption spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
RNAA	Radiochemical neutron activation analysis
MIBK	Methyl isobutyl ketone
HCl	Hydrochloric acid
HNO <sub>3</sub>	Nitric acid
LED	Light-emitting diode

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### Author contributions

BS contributed to guidance, planning and executing the analytical work, preparation and submission of manuscript. MK assisted in the analytical work and preparation of manuscript. AA Patwardhan was involved in the guidance.

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