

Estimation of Ti, Zr, Nb, Hf, Ta, Th and U in beach placers and ferrodiorites by inductively coupled plasma-mass spectroscopy using lithium metaborate fusion digestion technique

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Results are presented for the determination of Ti, Zr, Nb, Hf, Ta, Th and U in beach sand from Tamil Nadu coast and ferrodiorites from Bolangir District, Orissa, along with three certified reference materials, viz. AC-E, NIM-L and STM-1 by inductively coupled plasma-mass spectroscopy. Samples were decomposed by fusion with lithium metaborate (LiBO₂) and dissolution of bead in dilute nitric acid. The method described here is rapid and sample preparation is straightforward. This study critically evaluates results obtained from two sample digestion methods: LiBO₂ fusion and open vessel HF–HNO₃–HClO₄ digestion, and illustrates that LiBO₂ fusion is more effective for recoveries of high field strength elements and refractory minerals. Accuracy and precision achieved by this method of analysis were evaluated by replicate analyses of reference samples together with beach sands and ferrodiorite samples. The precisions obtained are <3% RSD in majority of the cases, with comparable accuracies.

Keywords: Beach placers, ferrodiorites, fusion digestion, lithium metaborate, refractory minerals.

THE overall success of any analytical procedure depends upon many factors, including proper sample preparation, appropriate sample dissolution and adequate separation and isolation of target analytes. In recent years, inductively coupled plasma-mass spectrometry (ICP-MS) has proven to be the most powerful technique for the estimation of trace and ultra-trace elements in a variety of geological materials¹. Fusion of rock samples with lithium metaborate (LiBO₂) in glassy carbon crucibles results in the formation of glasses which are readily soluble in dilute nitric acid. This procedure is effective for the dissolution of major rock-forming silicates as well as many accessory minerals^{2,3}. High field strength elements (HFSE) such as Nb, Ta, Zr, Hf and refractory elements such as Ti, Zr, Th and U are rarely determined in geological materials as a

group by a single analytical method due to their resistiveness to many decomposition procedures and their refractory nature. Even microwave digestion methods were found to be ineffective in the case of such samples⁴. Fusion digestion technique has been advocated as the preferred method for the effective decomposition of refractory materials.

Recent studies show that India has large reserves of beach-sand minerals in the coastal stretches around the country. Beach and stream placers commonly contain both rutile and ilmenite, associated with other heavy minerals such as magnetite, monazite, zircon, garnet, staurolite and sillimanite. Because of their hardness (above 5 on Mohs scale) and their resistance to chemical weathering, these tend to survive various geological processes, beginning with comminution of the source rock and ending with the sorting of heavier minerals by moving water, and concentration in placer deposits. Economically viable concentrations mostly occur in beach placer deposits and a few massive ore bodies in igneous and metamorphic provinces. Exploration studies of these minerals require accurate and precise estimation of Ti, Zr, Nb, Hf, Ta, Th and U in a large number of samples in order to have a better understanding of the mineralogy, geochemistry, and economic implications and radiological significance of these beach placer deposits.

In addition, trace-element discrimination studies for understanding the tectonic relationship between wide spectrums of co-magmatic igneous rocks, demand accurate and precise estimation of HFSE. Indian Proterozoic anorthosites are bordered by a spectrum (jotunite–mangerite–ferrodiorite) of fine-grained mafic rocks⁵. These rocks have high concentrations of HSFE and REE, geochemically resemble Lunar KREEP, and are supposed to represent the residual liquid of anorthosite crystallization. Unusually high Zr values ($\approx 5000 \mu\text{g/g}$) are reported from the ferrodiorites of Bolangir anorthosite⁶. The amount of REE in ferrodiorite from Bolangir (1000 times that of chondrite) is indicative of extreme fractionation processes that produced two contrasting rock types in terms of Zr content (anorthosite: 10–100 $\mu\text{g/g}$; ferrodiorite: 4000–6000 $\mu\text{g/g}$). Thus, to model the tectonics and fractionation processes that might have operated in the Proterozoic, one needs extremely accurate determination of Zr present in the rocks, as they are the storehouse of REE as Zr and REE are closely associated in geological processes.

Sample dissolution is a major hurdle in such studies because of the refractory and resistive nature of such rocks. Estimation of elements such as Ti, Zr, Nb, Hf, Ta, Th and U is also problematic using conventional instrumental methods such as flame atomic absorption spectrometry and X-ray fluorescence spectrometry, because of insufficient detection limits and accuracy offered by these techniques.

In this study, an attempt has been made to compare two dissolution techniques, viz. (i) fusion dissolution method

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Table 1. Description of international reference materials and samples studied

Source	Name	Material
US Geological Survey, Denver, USA	STM-1	Nephelene syenite
Council for Mineral Technology, Republic of South Africa	NIM-L	Lujavrite
IWG-GIT	AC-E	Granite
South of Bolangir, near Kansara	580, 592	Ferrodiorite
North of Bolnagir, near Loisinga	599, 597	Ferrodiorite
Tamil Nadu coast	1, 2, 3	Beach sand

using lithium metaborate flux in glassy carbon crucibles and (ii) conventional open acid digestion using different combinations of mineral acids in a PTFE vessel and estimation by ICP-MS. The ultimate aim is to establish a methodology for the most accurate and precise determination of Ti, Zr, Nb, Hf, Ta, Th and U in beach placers and ferrodiorites.

Three certified reference materials (CRMs), STM-1, NIM-L and AC-E, were taken together with the samples from beach placers of Tamil Nadu coast and ferrodiorites from Bolangir District, Orissa. Descriptions of these CRMs and samples are given in Table 1. Three sets of samples were prepared in each case.

A Perkin Elmer SCIEX[®], model 6100 ELAN DRC II ICP-mass spectrometer (Concord, Ontario, Canada) was used throughout. The sample introduction system consisted of a standard Meinhard[®] nebulizer with a cyclonic spray-chamber. All quantitative measurements were performed using instrument software (ELAN[®], version 4.0). Several well-known isobaric interferences were programmed, and the corrections automatically applied. Instrumental and data acquisition parameters are furnished in detail elsewhere⁷. Calibration was performed using STM-1 to minimize matrix and other associated interference effects, while NIM-L and AC-E were used to check the precision and accuracy of the analysis. RSD was found to be <3% in majority of the cases. External calibration procedure has been adopted for analysis. Rh was used as an internal standard.

Electronic grade HF, analytical reagent (AR) grade HClO₄, distilled HNO₃ and HCl, and lithium metaborate (AR grade) were used during sample preparation. Millipore purified water (18 M Ω) was used in all investigations. Glassy carbon crucibles (10 ml) were obtained from CARBONE, USA for lithium metaborate fusion.

Let us consider the open acid digestion method for sample preparation. About 0.05 g of sample was taken in PTFE teflon beakers. Each sample was moistened with few drops of ultra pure water. Then 10 ml of acid mixture (containing 7 : 3 : 1 HF : HNO₃ : HClO₄) was added to each sample. The samples were swirled until completely moist. The beakers were then covered with lids and kept overnight for digestion after adding 1 ml of 5 μ g/ml Rh solution (to act as an internal standard). The following day, the beakers were heated on a hot plate at ~200°C for about 1 h, the lids were removed and the contents were

evaporated to almost dryness until a crystalline paste was obtained. Then the remaining residues were dissolved using 10 ml of 1 : 1 HNO₃ and kept on a hot plate for 10 min at gentle heat (70°C) for dissolving all suspended particles. Finally the volume was made up to 250 ml with deionized water (18 M Ω) and stored in polyethylene bottles.

In the lithium metaborate fusion method of sample preparation, 0.05 g of sample and 0.25 g of lithium metaborate were weighed together, mixed thoroughly, transferred into a glassy carbon crucible (10 ml), and fused at 1050°C for 30 min in a muffle furnace. The crucible was cooled and the separated bead transferred into a beaker with 25 ml of 5% HNO₃ solution containing 1 ml of 5 μ g/ml of Rh to act as internal standard. The solution was continuously stirred with a magnetic stirrer for about 20 min for complete dissolution of the bead. The solutions were made up to 250 ml with deionized water (18 M Ω) and filtered to remove any suspended carbon particles and stored in 60 ml polyethylene bottles.

Accuracy of the ICP-MS measurements ultimately depends on the calibration of the instrument for individual elements, as most of them suffer from isobaric overlaps of metal oxides, doubly charged ions and other common molecular ion interferences. The isotopes used for measurement were carefully selected to avoid all the above possible interferences. In order to compensate for the signal drift due to changes in nebulizer efficiency, matrix-induced suppressions and enhancement effects⁸ and for minimizing mass discrimination and space-charge effects, ¹⁰³Rh was used as a single internal standard, as the concentration of this element was found to be at insignificant levels (<30 ng/g) in the samples investigated. Several studies have revealed that a single internal standard is sufficient for accurate measurement of trace and ultra-trace elements in geological samples^{7,9}.

Solutions containing >5% acid result in substantial erosion of the cone surface and in the geometry of the aperture itself. Use of relatively smaller quantities of high purity acids and other reagents led to lower blank values and resulted in sub-ng/ml detection limits for all elements investigated.

In order to overcome matrix effects that are generally observed during the analysis of geological samples, several methods can be used. Dilution of the sample, use of internal standard and matrix-matched reference samples for calibration, are some of the effective ways for this.

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Table 2. Concentration ($\mu\text{g/g}$) of trace elements in STM-1, NIM-L and AC-E determined by ICP-MS using open acid and fusion digestion methods

Analyte	Mass no.	STM-1			NIM-L			AC-E		
		Open digestion	Fusion digestion	CV	Open digestion	Fusion digestion	CV	Open digestion	Fusion digestion	CV
Ti (% TiO ₂)	48	0.12 ± 0.01	0.13 ± 0.00	0.14	0.38 ± 0.02	0.48 ± 0.01	0.48	0.06 ± 0.00	0.10 ± 0.00	0.11
Zr	90	1002.36 ± 60.1	1208.8 ± 14.51	1210.0	4500.3 ± 225	10964 ± 164	11000	689.08 ± 34.45	776.52 ± 9.36	780.0
Nb	93	253.11 ± 12.7	267.14 ± 4.27	268.0	895.23 ± 53.71	951.23 ± 15.22	960	99.12 ± 6.15	109.11 ± 1.42	110.0
Hf	178	23.22 ± 1.4	27.42 ± 0.55	28.0	175.32 ± 9.64	186.32 ± 3.73	190	22.32 ± 1.29	28.56 ± 0.60	27.9
Ta	181	15.25 ± 0.9	18.2 ± 0.36	18.6	17.89 ± 1.07	20.20 ± 0.61	22	9.89 ± 0.59	6.7 ± 0.20	6.4
Th	232	22.35 ± 1.3	30.51 ± 0.55	31.1	56.23 ± 3.04	62.65 ± 2	66	15.32 ± 0.80	18.23 ± 0.58	18.5
U	238	5.77 ± 0.3	8.83 ± 0.18	9.1	12.23 ± 0.73	15.11 ± 0.53	14	0.03 ± 0.00	4.56 ± 0.18	4.6

CV, Certified values (after Govindraju¹⁰).

Table 3. Concentrations ($\mu\text{g/g}$) of trace elements in beach sand from Tamil Nadu coast determined by ICP-MS using open acid and fusion digestion methods

Analyte	Mass no.	Sample 1		Sample 2		Sample 3	
		Open digestion	Fusion digestion	Open digestion	Fusion digestion	Open digestion	Fusion digestion
Ti (% TiO ₂)	48	15.2 ± 0.91	21.68 ± 0.43	18.25 ± 1.10	25.40 ± 0.51	9.56 ± 0.57	13.49 ± 0.27
Zr	90	3070.3 ± 153.5	9673 ± 116	4948.2 ± 296	8859 ± 221	1368.7 ± 75.2	3119.4 ± 49.91
Nb	93	2990.8 ± 134.5	3660.85 ± 54.91	1456.8 ± 80.13	1785.6 ± 46.43	671.01 ± 30.20	1021.2 ± 21.45
Hf	178	102.09 ± 3.57	259.52 ± 6.75	153.72 ± 7.99	245.3 ± 7.85	46.16 ± 2.59	87.08 ± 2.70
Ta	181	311.95 ± 16.22	450.45 ± 15.77	143.5 ± 7.32	236.5 ± 8.99	19.14 ± 1.38	25.65 ± 1.0
Th	232	2266.1 ± 72.5	4253.3 ± 110.59	2120.2 ± 97.53	4156.7 ± 49.8	1161.2 ± 48.7	2012.8 ± 56.3
U	238	21.68 ± 1.13	42.75 ± 2.14	3.043 ± 0.16	41.35 ± 1.86	0.72 ± 0.04	19.64 ± 0.55

Knowledge of sample composition and sample dissolution helps predict potential spectral interferences. The isotopes chosen for measuring different elements in this work are relatively free from potential polyatomic, isobaric and doubly charged ion interferences. Choosing of STM-1 as a calibration standard helped in minimizing the matrix and associated interference effects.

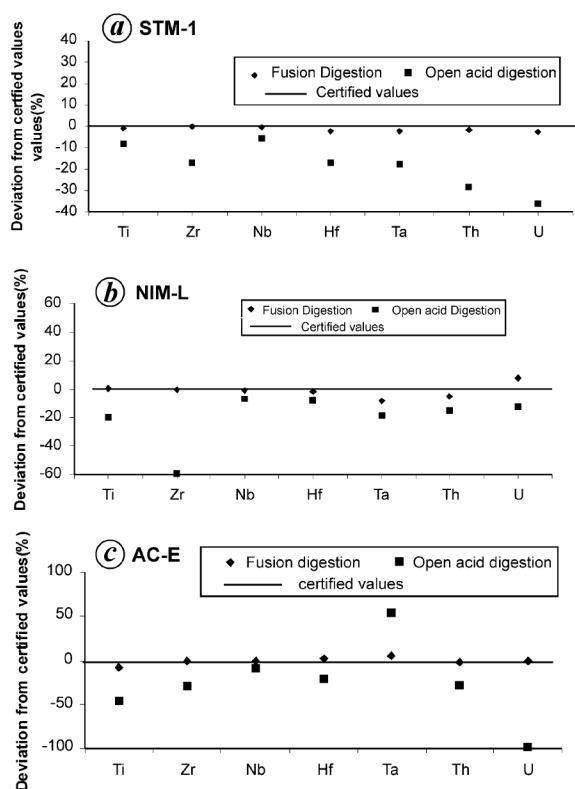
Ti, Zr, Nb, Hf, Ta, Th and U were analysed by ICP-MS for three international reference materials, STM-1, NIM-L and AC-E, together with beach-sand placer deposits of Tamil Nadu coast and ferrodiorites of Bolangir. Comparative results using both digestion techniques are given in Tables 2–4. The measured concentration of each element was compared with the available reference values¹⁰.

Despite the introduction of relatively high total dissolved solids (TDS) during sample preparation, which may restrict the quantification of some trace elements by ICP-MS¹¹, in the present study alkali fusion was found to be an useful alternative technique capable of decomposition of refractory minerals. In this study, an attempt has been made to reduce the TDS by taking 50 mg of sample and 250 mg of flux and diluting the sample after dissolution to

250 ml, which leads to 0.12% TDS only. These levels of TDS are tolerable by ICP-MS. This is effective when the number of samples taken in a batch is reasonably small (present study: 12). Investigations carried out by us on the stability of the standard and sample solutions of up to 0.12% TDS indicated that these solutions are extremely stable over a period of three months with respect to the elements investigated like Ti, Zr, Nb, Hf, Ta, Th and U. STM-1, NIM-L, AC-E, and samples of beach sand and ferrodiorites were fused with LiBO₂ in glassy carbon crucible at 1050°C. This was followed by HNO₃ treatment. The results show that the combined LiBO₂ fusion and HNO₃ acid digestion is an effective decomposition technique for trace elements, specially for Ti, Zr, Ta, Hf, Nb, Th and U. The average accuracy (compared with reference values) of trace elements for STM-1, NIM-L and AC-E was 1.3%, 1.1% and 0.6% respectively, with average spread of ±2% (Figure 1 a–c). Fusion digestion technique has many advantages over the conventional open acid digestion method: it does not require dangerous HF; dissolves all common rock-forming minerals, including zircon and chromite; all samples can be processed as a batch through

Table 4. Concentration ($\mu\text{g/g}$) of Zr in ferrodiorites from Bolangir District, Orissa determined by ICP-MS using open acid and fusion digestion methods

Analyte	Mass no.	SI no. 580		SI no. 592		SI no. 597		SI no. 599	
		Open digestion	Fusion digestion	Open digestion	Fusion digestion	Open digestion	Fusion digestion	Open digestion	Fusion digestion
Zr	90	280.32 \pm 5.88	4056.3 \pm 85.1	126.605 \pm 6.96	5235.7 \pm 130.8	208.5 \pm 9.3	3987.9 \pm 63.8	156.31 \pm 10.16	4174.7 \pm 79.3

**Figure 1 a-c.** Deviation of values of open acid and fusion digestion techniques from certified values.

each step; and fast in the sense that a large number of samples can be made ready for analysis in a couple of days. Although LiBO_2 fusion is a powerful decomposition technique for geological materials by ICP-MS, this method precludes the determination of volatile elements such as Sn, Sb, Tl and Pb due to high fusion temperature (1050°C). Though fusion procedure increases salt concentration, sometimes resulting in poor detection limits and need for frequent cleaning of the cones, nebulizer and spray chamber, in the procedure adopted in the present study, the TDS is extremely low and the above problems were not encountered. The use of high purity fusion flux resulted in extremely low blanks and detection limit did not suffer much when compared to the open acid digestion method. One major disadvantage of this method is that it is not possible to analyse Li and B in the samples for months by

ICP-MS because of the memory effects of these elements in the sample nebulization system.

On the other hand, open acid digestion method with HF, HNO_3 and HClO_4 at elevated temperature followed by evaporation to remove silica and fluoride, enabled most concentrated solutions to be analysed by ICP-MS. However, in the present study, it has been observed that the recoveries of Zr, Nb, Ta, Hf, Ti, U and Th by open acid digestion method is extremely low and incomplete (Tables 2–4; Figure 1 a–c).

These results suggest that for the determination of Zr, Nb, Ta, Hf, Ti, U and Th in beach sands and particularly Zr in ferrodiorites, it is essential to dissolve the samples by fusion digestion technique before ICP-MS analysis.

This study demonstrates that trace elements like Zr, Nb, Ta, Hf, Ti, U and Th can be determined at the ng/g and sub-ng/g levels in geological material at the precision and accuracy required for geochemical studies using lithium metaborate dissolution and ICP-MS analysis. The method is simple, rapid and effective. The data obtained on some of the international reference materials in this study compare well with available certified values. The relative error was found to be within $\pm 3\%$. The accuracy and precision achieved in majority of the cases was found to be $< 3\%$ RSD, suggesting that the data obtained by ICP-MS for the elements, viz. Zr, Nb, Ta, Hf, Ti, U and Th in international reference materials and the samples analysed from beach placers of Tamil Nadu and ferrodiorites from Bolangir District were best suited for geochemical interpretations.

Results of two different digestion procedures show that geological samples containing refractory and HFSE minerals should be digested using lithium metaborate fusion digestion. This study also illustrates the importance of careful consideration of the dissolution step when analysing geological materials, especially refractory minerals by ICP-MS.

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Dechlorination of chlorobenzoates by an isolated bacterial culture

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A range of chlorobenzoates is produced as dead-end metabolites during the microbial degradation of chlorinated aromatic compounds, including polychlorinated biphenyls (PCBs) and some herbicides. Hence studies on the microbial degradation of composites of chlorobenzoates are important for developing an effective bioremediation technology. An isolated bacterial culture had the ability to tolerate and grow in the presence of 2-chlorobenzoate (2-cba), 3-chlorobenzoate (3-cba), 4-chlorobenzoate (4-cba), a mixture of these chlorobenzoate isomers, 4-chloro,2-nitrobenzoate (4cnb) and chlorobenzene (cbz) using benzoate as the growth substrate. The microbial culture was able to dechlorinate all the above-mentioned chloroaromatics as well as their mixture to the extent of 50–75% under aerobic conditions. The rate of dechlorination followed the

order mixture >3-cba >4-cba >2-cba, with maximal release of 60, 75, 60 and 50 ppm of free chloride respectively, in the presence of 0.6% benzoate. Dechlorination appeared to begin at the end of the exponential growth phase and followed a linear course until the end of the lytic phase. The dechlorinating property of the isolated bacterial culture enabling it to act on mixtures of chlorinated benzoates in the presence of growth substrates such as benzoate may be useful for remediation of sites contaminated with PCB. To our knowledge the isolated bacterial culture is one of the few versatile strains to biotransform a variety of chlorinated aromatic compounds and their mixture through initial dechlorination.

Keywords: Bacterial culture, biodegradation, chlorobenzoates, dechlorination.

CHLOROBENZOATES are produced as metabolites during the microbial degradation of chlorinated herbicides and polychlorinated biphenyls (PCBs), and persist in contaminated areas as dead end-products¹. Reports have shown that the efficiency of biodegradation of monochlorinated biphenyls can be increased by the presence of bacteria that can degrade chlorobenzoates directly or by co-metabolism^{2,3}. Thus enhancing the efficiency of chlorobenzoate degraders and enrichment of their population is the key to successful bioremediation of PCB under *in situ* or *ex situ* conditions. Biodegradation of some individual mono- and dichlorobenzoates has been studied using pure or mixed microbial cultures. For example, *Pseudomonas aeruginosa* JB2 and *Pseudomonas putida* p111 have been shown to degrade 2-chloro, 3-chloro, 2,3-dichloro, 2,5-dichloro and 2,3,5-trichlorobenzoates via chlorinated catechols as central intermediates^{4,5}. However, few reports are available on the degradation of mixtures containing isomers/classes of chlorobenzoates. Commercial PCBs are available only as mixtures of several congeners thereby leading to the formation of range of a chlorobenzoates in PCB-contaminated zones through biotransformation activities. Thus the study of factors influencing the rates and extent of biodegradation of a mixture of chlorobenzoates is relevant.

In the present investigation we have evaluated the capability of an isolated aerobic bacterial culture to dechlorinate 2-, 3- and 4-chlorobenzoates (2-cba, 3-cba and 4-cba respectively), 4-chloro,2-nitrobenzoate (4cnb) and chlorobenzene (cbz) either singly or as mixtures, since these are the simplest model compounds for investigating the degradation of chloroaromatics in soil or water. The rate and extent of dechlorination of individual monochlorobenzoates or their mixtures were monitored in the presence and absence of growth-supportive substrate, benzoate. Also, the study involved relating the position of chlorine atom on the ring and effects of other substituents on the rate and extent of release of halogen from mono-chloroaromatic compounds.

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