Available online at www.sciencedirect.com
ScienceDirect
Fuel 87 (2008) 1469–1477
FUEL
www.fuelfirst.com

Determination of rare earth elements in Niger Delta crude oils by inductively coupled plasma-mass spectrometry

A. Akinlua [a,*], N. Torto [b], T.R. Ajayi [c]

[a] Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria
[b] Department of Chemistry, University of Botswana, P/Bag UB 00704, Gaborone, Botswana
[c] Department of Geology, Obafemi Awolowo University, Ile-Ife, Nigeria

Received 5 July 2007; received in revised form 8 September 2007; accepted 18 September 2007
Available online 11 October 2007

Abstract

A profile for rare earth elements (REE) of crude oils from the offshore – shallow water and onshore fields in the Niger Delta, analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) is reported. The oil samples were prepared for ICP-MS measurement by acid digestion into colourless aqueous solution. The analysis method was validated using standard reference materials SLRS-4 and NIST-1640. Results showed percentage recovery values that ranged from 81.8% to 115.4% for Co, Cu, Fe, Mn, Ni, Sb and U and from 98.8% to 104.7% for Co, Cu, Fe, Mn, Ni and Sb. The magnitude of deviation recorded in SLRS-4 for Co and Fe suggests that it may not be a suitable standard for these elements using the ICP-MS method outlined in this study. The concentrations of the detected REE; La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er and Yb ranged from 0.01 to 1.58 ppb with an average of 0.98 ppb (%RSD < 5) for the oil samples analyzed. Light REEs (LREE) were identified in all the oil samples while heavy rare earth elements (HREE) were identified in offshore oil samples only. LREE patterns constructed from chondrite-normalized values for the oils show some similarities among the oils, which suggest common origin of the oils and that the REE got into the oils from similar source. While those with different chondrite-normalized REE patterns suggest different source input of the REE. This indicates that REE will be a useful tool in oil–oil correlation. Statistical evaluation of these oils by cluster analysis using the REE as variables clearly discriminated according to their geographic sources. Biodegradation has pronounced effect on the concentration of REE in oils. Therefore, REE contents of oils will be useful in oil classification. ICP-MS proved to be a versatile method for the determination of rare earth elements in Niger Delta oils.

Keywords: Rare earth elements; ICP-MS; Oil; Niger Delta

1. Introduction

Qualitative and quantitative determination of trace element contents of crude oil is important in petroleum exploration. Trace element contents will enable prediction of the crude oil origin, maturity, migration and type or family. Trace elements are source of environmental pollution; some of them cause catalytic poisoning and corrosion of the turbines and refining columns. Trace elements in oils have been used for classification of oils [1], environment impact assessment [2,3], and oil to oil and oil to source rock correlation [4].

Different analytical techniques have been used to analyse trace element contents of crude oils. Lang et al. [5] and Hardway et al. [6] used atomic absorption spectrometry and related techniques to determine trace elements in crude oils. Algadi and Al Swaidan [7] determined vanadium in crude oil by inductively coupled plasma-mass spectrometry. Sequential injection analysis – inductively coupled plasma-mass spectrometric method had also been used to determine lead, nickel and vanadium in crude oil [8]. Trace metals in crude oils from different basins in the

* Corresponding author. Tel.: +234 8029593278.
E-mail addresses: aakinlua@oauife.edu.ng, stevesanya@yahoo.com (A. Akinlua).

0016-2361/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.fuel.2007.09.004

world have been determined by neutron activation analysis [9,10]. Hardway et al. [6] gave a succinct overview of the application of spectrometric techniques, which includes ICP-MS, ICP-AES, GFAAS and FAAS for the determination of trace metal contents in crude oils.

Limited data has been published on transition metals of Niger Delta crude oils [2,3,11,12]; however no study has been reported on rare earth elements distribution in crude oils. All the reports on the trace metal contents of Niger Delta oils showed that they are present in relatively low concentrations.

Given the reports in literature for analysis of transition metals, ICP-MS was found to be the most suitable technique for the determination of rare earth element (REE) contents of Niger Delta oils because it exhibits high sensitivity and accuracy, with high sample throughput. ICP-MS also allows rapid simultaneous multi-element determination of trace metals in crude oil samples.

The accuracy and detection limits of the ICP mass spectrometer are usually degraded when high concentrations of organic solvent are injected into the plasma. The introduction of organics into the plasma also leads to the formation of carbon-containing ions such as C_2^+, CO_2^+, and ArC^+ [13]. These ions create interferences in the elemental mass spectrum and can lead to compromise of trace level analyses of certain elements. These problems can be avoided by limiting the input of organic carbon to the plasma.

There are a number of techniques for eliminating the problems associated with organic matrices. The direct dilution of crude oils and petroleum based materials with an organic solvent is one of most an attractive sample preparation methods because it is rapid and simple [14,15]. The disadvantages of this technique include analyte signal suppression and hardware modifications to the instrument are required to utilize this technique.

Acid digestion of crude oil produces aqueous solutions that are suitable for ICP-MS instrumentation. The matrix effects are minimized, allowing the use of standard calibration curves, which accommodates high sample throughput. Acid digestion sample preparation procedure provides a good means of reducing organic load and therefore eliminates the elaborate mechanisms for removing solvent vapours from the aerosol stream. This paper describes an acid digestion sample preparation procedure that makes the oil available as aqueous solution that is suitable for ICP-MS instrumentation.

In this study, a rapid, reliable and accurate method of determination of rare earth element contents of crude oils was developed based on inductively coupled plasma-mass spectrometry (ICP-MS).

2. Experimental

2.1. Samples

Oil samples from offshore – shallow water (within longitude 4°10′E–4°40′E and latitude 5°35′N–5°45′N) and onshore (within longitude 5°16′E–5°18′E and latitude 5°40′N–5°41′N) fields in the western Niger Delta sedimentary basin were selected for this study. The location map for sampling is as presented in Fig. 1.

2.2. Reagents

All of the chemicals and reagents used for this analysis were of analytical-reagent grade and as specified by the Committee on Analytical Reagents of American Chemical Society. They include tetraoxosulphate (VI) acid, 30% hydrogen peroxide and ICP-MS standard of various elements determined in this study.

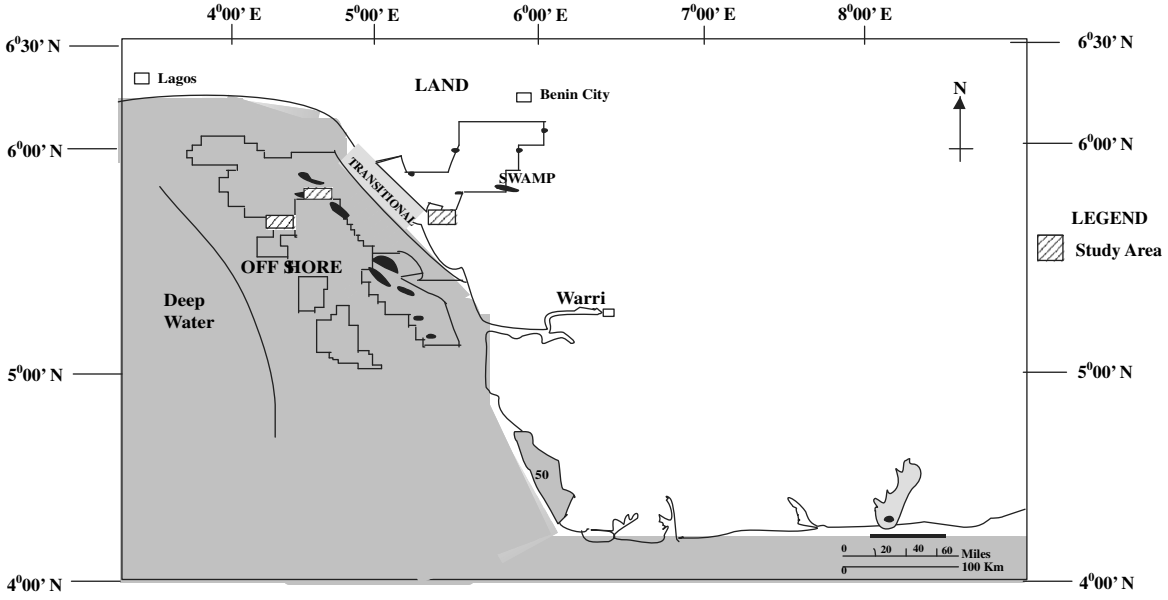

Fig. 1. Map of Niger Delta showing location of study.