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Subcritical water extraction of trace metals from petroleum source rock

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ABSTRACT

The extraction of trace metals from petroleum source rock by superheated water was investigated and the conditions for maximum yield were determined. The results showed that no significant extraction was attained at 100 °C but the extraction was enhanced at higher temperatures. The optimum temperature for superheated water extraction of the metals from petroleum source rocks was 250 °C. Extraction yields increased with enhanced extraction time. Exhaustive extraction time for all the trace metals determined in this study was attained at 30 min. Comparison of results of leaching these trace metals by superheated water with those of acid digestion revealed that cadmium, chromium, manganese and nickel had better yields with superheated water while vanadium had better yield with acid digestion. The results showed that the temperature and kinetic rates have significant effects on superheated water extraction of metals from petroleum source rocks. The results also revealed that effective leaching of some metals from petroleum source rocks by superheated water can be achieved without any modification except for vanadium.

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1. Introduction

There is a need to quantify trace metal concentrations in source rocks because of their importance in the geochemical characterization of source rocks and basins. Trace metals have been used as geochemical tools to understand the depositional environments of sediments and source rocks [1–3]. Trace metals are useful to understand the source and thermal maturity of kerogen [4]. Trace metal concentrations and ratios have been found to be invaluable tools in oil–oil correlation and oil–source rock correlation studies [5–7]. A few studies on the integration of trace metal and biomarker data of source rocks are also available [1,3,8]. Refining and environmental considerations are other important reasons for the determination of metals in the petroleum industry. Some trace elements especially vanadium and nickel behave as catalyst poisons during catalytic cracking process in refining of crude oil. Metals are released into the environment during petroleum exploration and production and also during the refining of crude oil. To make a meaningful impact assessment, it is necessary to know the composition of the oils and also the source rocks from which the oils were generated.

In most of these studies, the trace metals were determined by either atomic absorption spectrometric method or inductively coupled plasma-mass spectrometric method. These analytical techniques require acid digestion prior to analysis. Apart from the fact that acids are corrosive and hazardous, the acid digestion method procedure is time consuming and severely limits the rate of sample throughput. Trace metal contamination from the acid reagents, digestion vessels, and airborne particulates can jeopardize the accuracy of the analytical results. Also, quantitative recovery of elements such as mercury, boron, and selenium could be compromised during hot acid digestion.

Therefore, an alternative method that is non-hazardous, environmentally friendly and that will not compromise the qualitative and quantitative recovery of the metals from the sample matrix is required and superheated water extraction (SHWE) is a potential alternative method. The method has been applied successfully for the extraction of organic compounds from different solid matrices [9–14]. Since metals are more soluble in water, even the organically bound metals in sediments should be amenable to the superheated water extraction. In previous work selected toxic metals have been successfully extracted from coal and sludge samples using superheated water at 180 °C and 250 °C [15–17] and Morales-Munoz et al. [18] used acidified pressurized hot water at 250 °C for the continuous extraction of cadmium and lead from plants. In this study, the extraction of some trace metals from petroleum source rocks by superheated water was carried out. The study was undertaken in order to determine the effects of temperature and time on the extraction yields of the metals and to establish the conditions for maximum yields of the metals from the superheated water extraction of petroleum source rocks in order to use the information for geochemical characterization. A previous study in this laboratory

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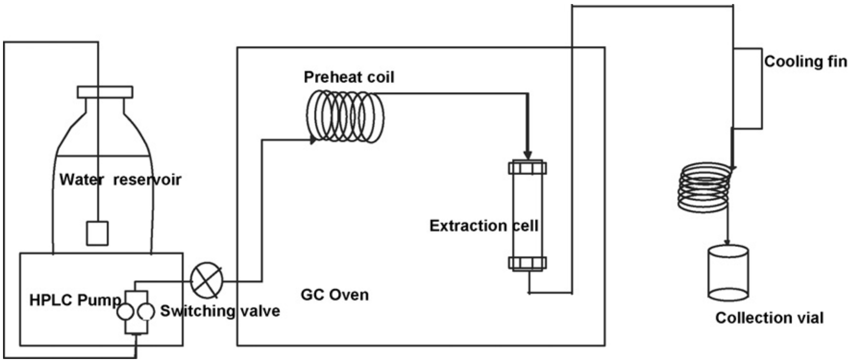

Fig. 1. Schematic diagram of superheated water extraction.

has examined the composition of the organic compounds extracted using this technique [19].

2. Experimental

2.1. Samples

Organic sedimentary rock samples, obtained from an oil field in Niger Delta, were characterized as Type II/III kerogen with a TOC of 1.63 wt%. The rock samples were pulverized, homogenized and passed through a 120 mesh screen. 2.5 g of sample was used for each superheated water extraction.

2.2. Chemicals

All of the chemicals and reagents used in this analysis were of analytical reagent grade. Water was deionized to 18 MΩ using an Elga Maxima purification unit (Elga Ltd. Wycombe, Bucks, UK)

2.3. Superheated water extraction

The superheated water extraction experiments were performed using the experimental set-up as shown in the schematic diagram (Fig. 1). The deionized water was sonicated for 1 h to remove dissolved air. The water was delivered at a constant flow rate of 0.5 mL min^{-1} by a Jasco PU-980 Intelligent HPLC pump (JASCO, Tokyo, Japan) through a stainless steel preheating coil of 1 m length and 0.17 mm I.D. to a stainless steel column (50 mm × 10 mm I.D.) used as an extraction cell, filled with a dry mixture of 2.5 g of rock sample. Stainless steel frits of 2 μm mesh size at the ends of the column contained the sample and prevented particulate matter from entering the water transfer lines. The extraction cell and the preheating coil were placed in a Philips PU 4500 gas chromatograph (GC) oven (Cambridge, UK), and maintained at a constant temperature. The water was passed vertically through the extraction cell for down-flow extractions. The extraction cell outlet was connected to a 2 m length of stainless tubing (0.17 mm I.D.) which provided back-pressure control, with cooling fins attached outside the oven to conduct heat away and cool the extractant to ambient temperature. The water extract was collected in a vial immersed in ice. Each superheated water extraction experiment was carried out in two stages; the static stage, which was undertaken for 10 min after the cell had been filled, followed by a dynamic stage during which the water was pumped at 0.5 mL min^{-1} for 10 min, 20 min, 30 min, 40 min and 50 min. The temperature was increased in steps of 50 °C from 100 °C to 300 °C at a pressure of more than 5.0 MPa which was sufficient to prevent the water from boiling. The organic compounds in the aqueous extract were removed by solid phase microextraction (SPME) with recovery of average of 93% *n*-alkanes which constitute bulk of the organics in the water extract and any residual organics were removed by liquid–liquid extraction with dichloromethane. The aqueous extract was then filtered by 0.2 μm filter paper before inductively coupled plasma-mass spectrometric (ICP-MS) analysis. Since there is no standard reference material for petroleum source rock, comparison with established standard acid digestion method was made for accuracy of the method. Acid digestion of the rock samples was achieved with 10 mL of aqua regia and 2 mL of 30% hydrogen peroxide at 110 °C for 5 h [20] and replicate extractions were compared with a blank digestion.

2.4. ICP-MS determination

The metals in the aqueous extract after removal of the organics were determined by inductively coupled plasma-mass spectrometry (ICP-MS) using Thermo Finnigan Element 2/XR (Thermo Electron Corporation) inductively coupled plasma-mass spectrometer. The ICP-MS was operated under the following conditions; RF incident power of 1.2 kW, plasma gas flow rate of 13 L min^{-1}, auxiliary gas flow at 1.4 L min^{-1}, nebulizer gas pressure of 40 psi, counting precision of 0.1, measurement time of 0.05 s and sample flow at 60 μL s^{-1}.

3. Results and discussion

Both the extraction temperature and the time are critical parameters and were investigated for the SHWE of trace metals from petroleum source rocks. The yields of characteristic metal ions from the rocks were determined by ICP-MS after extraction of organic components and filtration. The metals determined were mainly for petroleum exploration consideration.

3.1. Effect of extraction temperature

The extraction temperature was increased in steps of 50 °C from 100 °C to 300 °C. None of the metals showed significant extraction at 100 °C but as the temperature was increased, the yields of all the metals increased and then levelled off at a maximum yield (Fig. 2), which was a point of exhaustive extraction. The temperature for maximum yield for all the metals was 250 °C and further increasing the extraction temperature to 300 °C had little effect. The relative yield of the major component, manganese, correlates with the yield of this metal in crude oils and kerogens of the basin from which the rock samples were obtained. Manganese was present in significant abundant amount in the crude oils [21,22], while manganese was second most abundant after iron in the kerogens [4]. This metal is usually depleted in reducing environments and enriched in oxidizing environments [2].

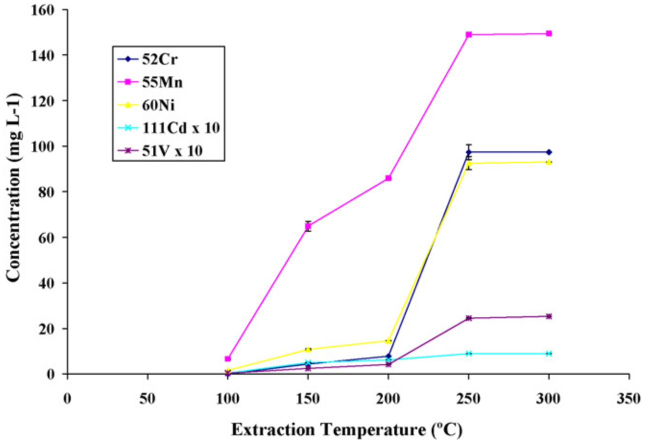

Fig. 2. Effect of varying the extraction temperature on the yields of Cr, Mn, Ni, Cd and V from petroleum source rock using superheated water extraction.

3.2. Effect of extraction time

To determine the effect of extraction time, extractions were performed using the temperature of 250 °C for 10 min, 20 min, 30 min, 40 min and 50 min as washout time. As shown in Fig. 3, as the time was increased, the yields of all the metals increased to a maximum around 30 min and further increasing the extraction time had little effect on the yields of the metals. These results suggest that the extractability of the metals from petroleum source rock by superheated water may be insignificant of the strength of their retention or their abundance in the rock matrix at higher extraction time greater than 30 min and extraction temperature greater than 250 °C. The last factor may explain why manganese, which had relatively high abundance compared to other metals, still had the same optimal extraction time with other metals.

Generally, increasing the extraction time above the maxima for different metals did not improve their extraction efficiency. Considering the overall results, an extraction time of 30 min was adopted for the metals determined in this study.

3.3. Extraction efficiency of SWE of trace metals from petroleum source rocks

Because of non-availability of certified standard reference material for petroleum source rock, the yields of trace metals from superheated water extraction and traditional acid digestion method were compared (Fig. 4); relatively high yields of cadmium, chromium, manganese and nickel were obtained compared to leaching of these elements by acid digestion, only vanadium had high yield with acid digestion. Ordinarily, acid may be stronger than water in solubilizing metal from rock but as the temperature of water increases its metal solubilizing strength increases. As water heats up, the molecules gain thermal energy, and overcome the hydrogen-bonded network present in normal liquid water. This results in some properties of water changing more than would usually be expected with temperature especially its solubilizing strength. For example, at 200 °C and above water starts behaving like organic solvents [23]. It is not surprising that its metal solubilizing strength is comparable to that of acid or even stronger for some metals at high temperature (Fig. 4). The difference in the results of vanadium from the SHWE and acid digestion suggests that leaching of this metal from petroleum source rock may be dependent on the chemical form in which it existed in the rock matrix. Therefore, SHWE of vanadium from petroleum source rock will require modification. Such modification may involve slightly acidifying the water, which we intend to investigate in more details and report in future.

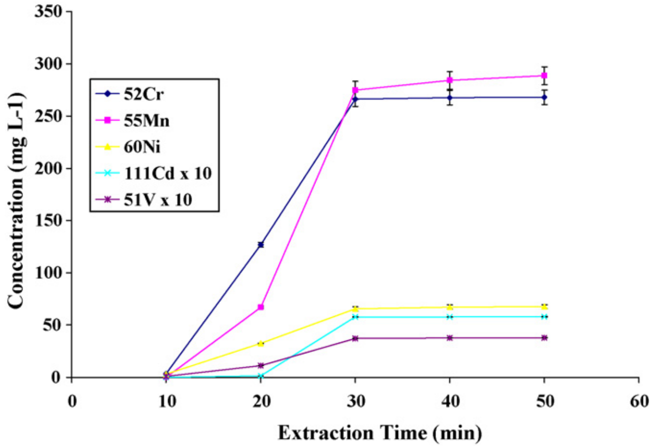

Fig. 3. Effect of varying the extraction time (dynamic mode) on the yields of Cr, Mn, Ni, Cd and V from petroleum source rock using superheated water extraction.

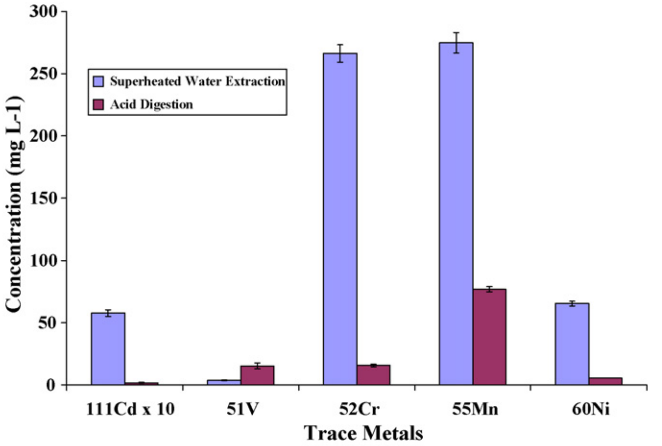

Fig. 4. Comparison of leachability of trace metals by superheated water and acid digestion from petroleum source rock.

4. Conclusions

The extraction efficiency of trace metals from sedimentary organic rock by superheated water was found to be strongly temperature and time dependent. The exhaustive extraction temperature for all the metals was reached at 250 °C. The optimal yields of all the metals determined in this study were obtained at 30 min. Superheated water extraction method is effective for the leaching of cadmium, chromium, manganese and nickel from petroleum source rock but not comparatively effective for vanadium; extraction of vanadium may require modification.

This study has proved that superheated water extraction is a robust environmentally friendly analytical technique for the extraction of some trace metals from petroleum source rock without any modification.

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