

## APPLICATION OF SULPHURIC ACID WET-ASHING PROCEDURE TO THE DETERMINATION OF SOME TRACE METALS IN CRUDE OIL

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**ABSTRACT.** The sulphuric acid wet-digestion technique has been applied to the determination of some trace metals in crude oil. A minimum acid ratio of 3.5 cm<sup>3</sup> per gramme of oil is required to obtain peak recovery for nickel, iron, calcium, magnesium, sodium, potassium, copper and zinc. The method is highly reproducible. Mean recoveries of sodium and nickel from a spiked sample were 95.3 and 92.3 % respectively. Results have been obtained for a wide range of crude oils and there is a good agreement with those obtained by the standard ashing procedure established by Institute of Petroleum.

### INTRODUCTION

Firm quantitative data on the metal content of crude oils are important from the refining standpoint, for formulating theories on the origin of petroleum and deriving relationship between crudes and geological strata (1). For example, knowledge of trace metal contents is useful in designing demetallation processes to remove metals such as nickel, vanadium and sodium, among others which act as catalyst poisons. Since the catalytic poisoning effects of some metals in crude oils on cracking catalysts were first discovered, numerous techniques have been described for the quantitative analysis of metals in petroleum (2), the most crucial step in these techniques being the sample preparation stage.

It is well known that metal ions are liable to losses during simple ashing of crude oils. Various attempts have therefore been made to overcome such losses. In particular, determinations after dilution with organic solvents are known to simplify analyses and overcome such losses (3-5). However, with the organic solvents, organometallic salts are frequently employed for calibration. These salts are often less readily available than inorganic salts and are more expensive or require accurate preliminary analyses which further increase the cost. Furthermore, their solutions are usually less stable (6), and results obtained depend on the type of compound used for calibration (7). Sometimes, anomalously low results are obtained (6). Oxygenated solvents and mixed solvent systems are usually used for application of aqueous inorganic salt standards, thereby making such analyses cheaper (8,9). Yet, flame problems are still common and the instrument must be suitable for the use of organic solvents.

On the other hand, incineration of oil with sulphur (10), or coking with either benzenesulphonic acid (11), p-xylenesulphonic acid (12) or sulphation with concentrated sulphuric acid either partial or total (13, 14) have been reported to prevent metal losses during ignition. For the total sulphated ash techniques, use of different ratios of concentrated sulphuric acid per gramme of oil for ashing has been described for different types of petroleum distillate fractions (15). Gamble and Jones (16) carried out an investigation on the effect of varying the ratio of sulphuric acid on the recovery of metals when analysing petroleum

distillates, and recommended a ratio of 1-2 cm<sup>3</sup> of the acid to one gramme of oil. The authors reported that neither higher ratios of the acid to oil distillate (up to 16 cm<sup>3</sup> g<sup>-1</sup>) nor an increased time of contact at low temperatures produced an increased recovery. To our knowledge there is no record of the Gamble and Jones type of investigation with crude oils. In this paper therefore, we report an extension of their work to the determination of some trace metals in some Nigerian and Venezuelan crudes.

## EXPERIMENTAL

*Reagents and apparatus.* Unless otherwise stated, all reagents were of analytical reagent grade. Doubly distilled water was used in the preparation of all aqueous solutions.

Standard stock solutions of 1000 ppm of Fe, Ni, Ca, Mg, Na, K, Cu and Zn were prepared from the chlorides (Na, K, Mg), nitrates (Ni, Cu), carbonate (Ca), oxide (Zn) or sulphate (as ammonium sulphate hexahydrate) (Fe).

A Pye Unicam SP 1900 atomic absorption spectrometer (AAS) equipped with mono-elemental hollow-cathode lamps and digital read-out was used for absorbance measurements, except for Na and K which were determined using a flame photometer. An air-acetylene flame was used. A 5% (w/v) lanthanum nitrate solution was used to minimize interference from oxy-anions such as phosphate, aluminate and silicate in the determination of calcium and magnesium. The crude oil samples analysed are shown in Table 1.

Table 1. Crude oil samples and sample codes.

Sample Code No.	Sample Name	Source
1	Mixed forcados light	ELF Nigeria Limited
2	Obaji medium	ELF Nigeria Limited
3	Brass Blend	Nigerian Agip Oil Company
4	Bonny light	Shell Petroleum Development Company
5	Bonny medium	Shell Petroleum Development Company
6	Venezuelan Crude	Kaduna Refinery

### *Standardization of procedure*

*Acid to oil ratio.* The effect of varying the ratio of volume of concentrated sulphuric acid to mass of sample on the metal recovery was examined using crude oil sample 1. This sample was mixed with varying ratios of concentrated acid to oil, coked, ashed and analyzed, to obtain the optimum acid to oil ratio for analysis.

*Heating procedure.* Previously recommended heating procedure involving the use of vycor dishes and heating from top with an infra red lamp (17) is known to take longer than a day for the oil to solidify. In this study an ordinary Pyrex beaker was found to be suitable. A fast and consistent evolution of fumes devoid of spattering was obtained by heating the oil-acid mixture on a heating mantle with constant swirling of the beaker during the vigorous reaction stage. Spattering was further prevented by reducing the mantle temperature when the reaction was very vigorous. After solidification of the oil, the mantle temperature was again increased. In order to ensure that sulphuric acid does not evaporate without bringing about the required conversion of the volatile elements, and in order to break the surface crust and ensure adequate mixing of the oil with the acid, a simple swirling of the beaker was found to be sufficient.

*Muffling temperature.* The charred carbonaceous residue obtained from heating

is usually reduced to ash by heating in a muffle furnace. In this study, Pyrex beakers were used and the muffling temperature of 500°C was adequate to ash all the carbon in the sample. At temperatures > 500°C ordinary Pyrex beakers get disfigured.

*Preparation of representative samples.* In crude oils particles are usually not evenly distributed and the distribution varies on standing with the larger particles settling to the bottom of the container. Crudes also contain sludge water. In order to ensure adequate mixing, the samples were heated on a steam bath for at least 30 minutes with vigorous shaking. Shaking was repeated before any portion was taken out with a dropper.

*Sample size studies.* Normally, as much sample should be used that will give enough ash for analysis. Earlier workers (17) using 0.5 cm<sup>3</sup> of concentrated sulphuric acid per gramme of oil for ashing, recommended the use of 100 g samples or increments thereof. This was mainly due to the inability to overcome volatilization of valuable components due to use of insufficient acid. However, the Institute of Petroleum (18) has recommended an upper limit of 30.0 g oil. In this study we have examined the use of 10, 15, 20 and 25 g of oil at an acid to oil ratio of 3.5 cm<sup>3</sup> g<sup>-1</sup>, using sample 1.

*Proposed procedure.* 20 g of the homogenized oil was placed in a 500 cm<sup>3</sup> beaker. 3.5 cm<sup>3</sup> of concentrated H<sub>2</sub>SO<sub>4</sub> per gramme of oil was added. The beaker was swirled gently. The oil-acid mixture was heated on a heating mantle initially at high temperature and swirling the beaker constantly. When the reaction was vigorous, the mantle temperature was reduced and swirling of the beaker continued until a solid, carbonaceous residue was produced. This required only about 25 minutes. Heating of the coke-like residue on the heating mantle with increasing temperature was continued until there was practically no evolution of fumes. The beaker with the solid was placed in a muffle furnace, the temperature was increased gradually until the coke was finally ashed at 500°C. The ash was digested with 20 cm<sup>3</sup> hydrochloric acid (1+1) over a steam bath until the volume was reduced to about 5 cm<sup>3</sup>. The solution was transferred quantitatively to a 25-cm<sup>3</sup> volumetric flask and diluted to volume with water. A reagent blank was prepared using an equal volume of concentrated H<sub>2</sub>SO<sub>4</sub>.

*Recovery studies.* Sample 6 was spiked with different concentrations of sodium and nickel added as cyclohexanebutyrate of the metal in amyl alcohol. The mixtures were then ashed and analyzed by the recommended method.

## RESULTS AND DISCUSSION

*Effect of varying ratio of acid to oil.* Fig. 1 shows that the amount of each metal determined from the ash increased initially with increasing volume of acid per gramme of oil until an optimum value was obtained. Variation of up to 15 cm<sup>3</sup> of acid per gramme of oil gave neither an increased recovery nor an adverse effect. However, at high ratios, the carbonaceous residue became very 'rubber-like' and was difficult to dry within a reasonable time required for routine work. A distinctive advantage of using the correct quantity of H<sub>2</sub>SO<sub>4</sub> in this process is that the amount of cokelike residue formed is very large, and, as in gravimetry, serious errors may not be encountered even if a small portion of the residue is lost at that stage due to poor handling. The curves in Fig. 1 show that the lowest quantity of the acid that gives a peak recovery for all the metals determined is about 3.5 cm<sup>3</sup> per gramme of oil.

*Effect of sample size.* The results given in Table 2 show that 20.0 g of oil was sufficient for optimum recovery in each case. This quantity compares favourably with the upper sample limit of 30.0 g of oil recommended by the Institute of Petroleum (18), and represents an improvement on 100.0 g recommended by some earlier workers (17).

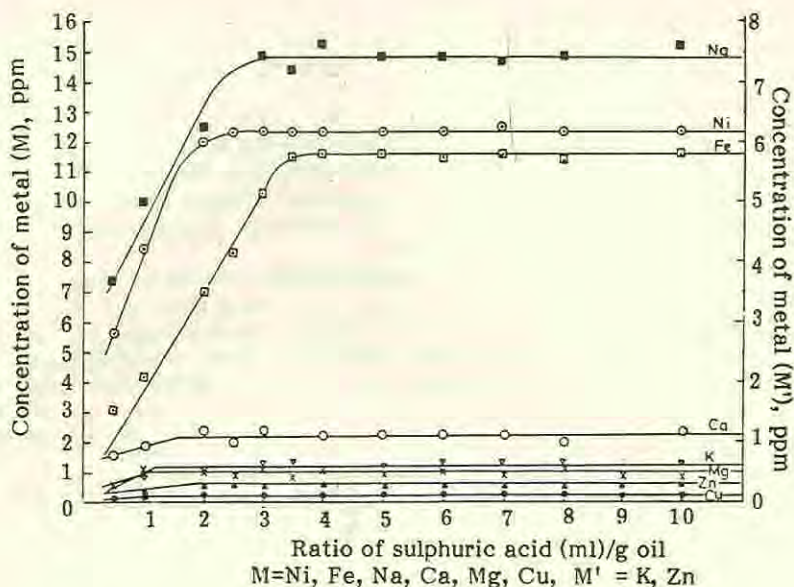


Fig. 1. Effect of ratio of sulphuric acid to mass of oil on metal recovery.

Table 2. Effect of sample size on metal recovery on ashing with  $H_2SO_4$  using sample No. 1.

Sample Size (g)	Metal concentration (ppm)							
	Ni	Fe	Ca	Mg	Na	K	Cu	Zn
10.0	10.1	11.2	1.7	0.5	13.0	0.5	0.2	0.3
15.0	12.4	11.6	2.0	0.7	14.4	0.6	0.2	0.3
20.0	12.3	11.6	2.2	1.1	14.8	0.6	0.2	0.3
25.0	12.3	11.6	2.1	0.9	15.0	0.6	0.2	0.3

**Reproducibility of proposed procedure.** The estimated standard deviations based on the mean of eleven determinations in each case (Table 3), are sufficiently low to suggest good precision of the proposed method.

**Recovery from spiking.** Results in Table 4 show mean recoveries of 95.3% and 92.3% for sodium and nickel respectively. The recoveries are quite good and well within acceptable limits for this type of analysis (19,20).

**Comparison of results from two methods.** Table 5 shows that results from the proposed method compare well with those from the Institute of Petroleum standard procedure (18). The results also indicate the wide variations in composition that may be expected. However, much of the literature is replete with information about nickel and vanadium in crude oils or petroleum distillates.

Very little has been done about sodium even though it is equally known to cause serious loss in catalyst activity when present in stocks charged to catalytic cracking units (21). Also, when present in residual fuel oil, sodium imparts corrosive properties and causes shortening of life of furnace tubes, turbine blades and other metal surfaces (22). This work has shown that sodium is available

Table 3. Reproducibility of the H<sub>2</sub>SO<sub>4</sub> ashing procedure using sample No. 1.

Element	Mean concentration (ppm)	Standard deviation (SD)
Ni	12.3	0.1
Fe	11.6	0.1
Ca	2.2	0.1
Mg	1.1	0.1
Na	14.0	0.1
K	0.6	0.0
Cu	0.2	0.0
Zn	0.3	0.0

Each reported value is a mean of 11 determinations.

Table 4. Recovery of sodium and nickel from spiked crude sample No. 6.

Element	Amount added (ppm)	Amount recovered (ppm)	Recovery (%)
Na	2.0	1.9	95.0
	10.0	9.4	94.0
	100.0	97.0	97.0
Ni	2.0	1.8	90.0
	10.0	9.2	92.0
	100.0	95.0	95.0

The metals were added as their cyclohexanebutyrate.

Table 5. Comparison of results obtained by proposed method with Institute of Petroleum method (IP 285/79/85).

Sample No.	Element	Concn. by proposed method (ppm)	Concn. by IP 285/79/85 method (ppm)	Sample No.	Element	Concn. by proposed method (ppm)	Concn. by IP 285/79/85 method (ppm)
1	Ni	12.3	12.2	4	Ni	3.3	3.6
	Fe	11.6	9.5		Fe	8.4	7.7
	Ca	2.2	3.0		Ca	5.9	8.3
	Mg	1.1	1.2		Mg	1.2	1.5
	Na	14.8	15.3		Na	47.0	35.0
	K	0.6	0.9		K	0.7	0.8
	Cu	0.2	0.2		Cu	0.1	0.1
	Zn	0.3	0.4		Zn	0.4	0.1
2	Ni	2.8	3.0	5	Ni	6.6	7.2
	Fe	3.4	3.0		Fe	7.8	7.6
	Ca	3.6	4.3		Ca	6.1	9.9
	Mg	0.7	0.9		Mg	2.7	1.5
	Na	11.1	7.8		Na	9.7	13.6
	K	0.6	0.7		K	1.0	1.3
	Cu	0.1	0.1		Cu	0.1	0.3
	Zn	0.3	0.5		Zn	0.2	0.2
3	Ni	1.8	1.7	6	Ni	20.3	19.8
	Fe	0.9	0.8		Fe	0.9	1.6
	Ca	5.0	8.9		Ca	N.D.	N.D.
	Mg	2.5	2.7		Mg	2.2	4.6
	Na	51.5	63.8		Na	16.1	16.3
	K	0.7	1.1		K	0.8	1.2
	Cu	0.1	0.2		Cu	0.1	0.1
	Zn	0.5	0.3		Zn	0.2	0.2

N.D. means "Not Determinable".

in proportions high enough to cause concern in both Nigerian and the Venezuelan crudes. The generally low values for the majority of the other elements

corroborate the findings of Coker (23) that Nigerian crudes have low metal contents, even though the latter author based his assertion only on results obtained for nickel and vanadium.

## CONCLUSION

It has been established that the sulphuric acid ashing procedure hitherto used mainly for the determination of trace metals in petroleum distillate fractions can also be applied to the determination of nickel, iron, sodium, potassium, calcium, magnesium, zinc and perhaps other metals in whole crudes. It is essential that the correct ratio of acid to crude be used. The proposed method reduced considerably the time required to solidify the oil during the sample preparation stage from over one day to about 25 minutes, and is therefore adequate for routine analysis.

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