PRJ, Vol. 4. (January 1992); P. 72–74, 2 FIG, 4 TABLES.

## Short Note

# DETERMINATION OF TRACE METALS IN SOME GAS OIL FRACTIONS OF LIBYAN CRUDE OILS BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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# تحديد العناصر في بعض قطفات وقود الديزل المنتج من النفط الخام الليبي بإستعمال الإمتصاص الذري (الكهروحراري)

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تم إستعمال جهاز الإمتصاص الذري (الكهروحراري) لتحديد آثار العناصر في قطفات وقود الديزل المنتج من النفط الخام الليبي. فقد تم تحديد كمية الحديد ، النيكل ، النحاس ، الفانيديوم ، الكروم والرصاص في هذه القطفات.

## INTRODUCTION

Trace metals in crude oil and their products are commonly determined by atomic absorption spectrophotometry. The presence of some metals (e.g. Ni, Cu, Fe, As) in the crude oil causes poisoning of the catalysts used in refining processes, and other metals (e.g. V) cause corrosion problems, thus reducing the efficiency of the refining plant [1–3]. On the other hand, the nature and level of metals in the oil can be used for identification of the source of the oil. The presence of copper in refined products promotes formation of gums and lacquers during heating or storage and thus accelerates the deterioration of these products and reduces the storage stability [4]. Vanadium concentration above 2 ppm in fuel oils can lead to severe corrosion turbine blades and deterioration of refractory furnace linings and stacks.

Most of the metallic species in petroleum products are present as volatile organometallic compounds, salts, fine metallic particles and coloidal suspensions.

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Atomic absorption trace methods [4] are known to determine the concentrations of trace metals in petroleum fractions. In many cases, to use atomic absorption equipment effectively, it would be necessary to destroy the organic matter and concentrate the metal content. The solution to the problem involved designing a simple method of decomposing the petroleum products' organic matter, while retaining the trace elements in an easily soluble flux, with a low blank, and solubilizing a maximum number of elements in one simple preparation.

Middleton and Stuckey [5] published work about dry ashing at 350°C with $HNO_3$, holding Ag, As, Cd, Co, Cr, Cu, Fe, Mo, Pb, Sr, and Zn. Gorsuch [6] published a study of recovery of fourteen different trace elements from organic material. He summarized some 250 investigations reported in the literature, to aid him in a choice of methods to study. The most common method found was direct dry ashing; second most common was wet digestion with nitric and sulphuric acids. Methods reported giving efficient trace element recovery, following destruction of organic matter, were dry ashing with sulphuric acid,

nitric acid, or magnesium compounds. An alternative approach arises from the comprehensive report by Gorsuch on the recovery of trace elements after wet and dry ashing. It has been shown [7] that all the wanted metallic elements are retained after dry ashing at 500°C provided a suitable ashing aid such as p-toluene sulphonic acid is employed. The metals are extracted from the residual ash with nitric acid, and cesium chloride is used as ionization buffer.

This paper presents the analysis of six trace metals in some gas oil range fractions obtained from Libyan crude oils by atomic absorption spectrophotometer using graphite furnace tube. p-toluene sulphonic acid was employed as ashing aid.

## EXPERIMENTAL

### Reagents and Materials

All chemicals used were of high purity analytical grade. Standard solutions of different elements of interest were prepared by appropriate dilution from stock standards supplied by VHG Labs, Inc, Manchester. High purity deionized water was used throughout the sample preparations. All solutions were stored in precleaned polypropylene containers. Export blend crude oil samples were collected at source and the appropriate fractions were collected from laboratory scale fractionation column. The fractions studied were 220–280°C and 280–340°C boiling ranges.

### Apparatus

Atomic Absorption Spectrophotometer (Varian AA 1475) coupled with Varian GTA-95 graphite tube atomizer was used throughout this study. The instrument has also facilities of background correction and automatic sampling. The unit contains Epson recorder (model RX-80) attached to the atomic absorption spectrophotometer. Varian high intensity, hollow cathode lamps were used for all the elements analysed. The GTA furnace operation conditions used for each element are shown in Table 1.

**Table 1. Conditions of Furnace Setting**

| Element | Wave length (nm) | Temperature Setting (in °C) | |
|---|---|---|---|
| | | Start temp. | Plateau temp. |
| Cu | 384.8 | 75–120 | 2300 |
| Cr | 357.9 | 75–120 | 2500 |
| Pb | 217.0 | 75–120 | 2000 |
| Fe | 248.3 | 75–120 | 2300 |
| V | 318.5 | 75–120 | 2700 |
| Ni | 232.0 | 75–120 | 2400 |

### Procedure

A known weight of about 20.000 g of sample was placed in a platinum crucible together with 1.0 g p-toluene sulphonic acid and then dry ashed in a muffle furnace at 500°C for 60–90 minutes. The residue was brought to room temperature. Then 10 ml of 25% nitric acid was added, warmed gently and filtered into 50 ml volumetric flask, washed with further 10 ml of 25% nitric acid, added 5 ml of 1% cesium chloride solution and finally made up to the mark with distilled water. The blank solutions were prepared for each sample in duplicate. Calibration solutions were prepared from stock standards to contain the same concentrations of nitric acid (5%) and cesium chloride (0.1%) as the sample solutions. Table 2 represents the experimental condition used for the determination of different elements in various samples.

**Table 2. Experimental Conditions for Determination of Different Elements**

| Element | Conc. range ($\mu g\, g^{-1}$) | Wave length (nm) |
|---|---|---|
| Cu | 0.0060–0.1400 | 324.8 |
| Cr | 0.0004–0.0100 | 357.9 |
| Pb | 0.0800–1.1000 | 217.0 |
| Fe | 0.0200–0.7000 | 248.3 |
| V | 0.0400–0.1000 | 318.5 |
| Ni | 0.0500–1.1000 | 232.0 |

The weight of the sample was taken accurately weighed about 20.0000 g in each sample.

## RESULTS AND DISCUSSION

The calibration plots of copper, chromium and iron were straight lines while for lead, vanadium and nickel were smooth curves. All plots pass through the origin. The calibration curves, as an example, for copper and lead are shown in Fig. 1a and Fig. 1b respectively.

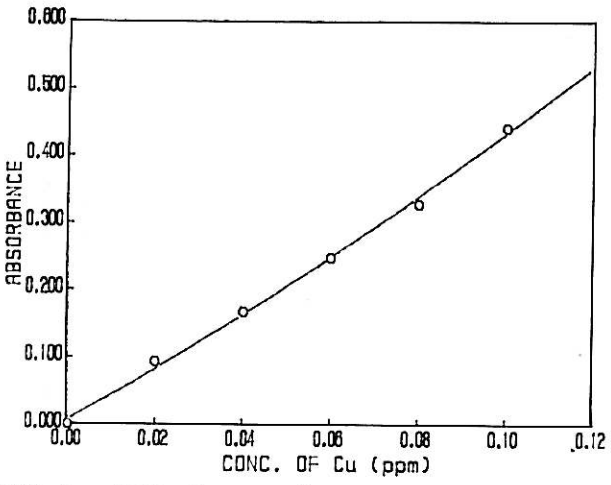



FIG. 1a. Calibration curve for copper.

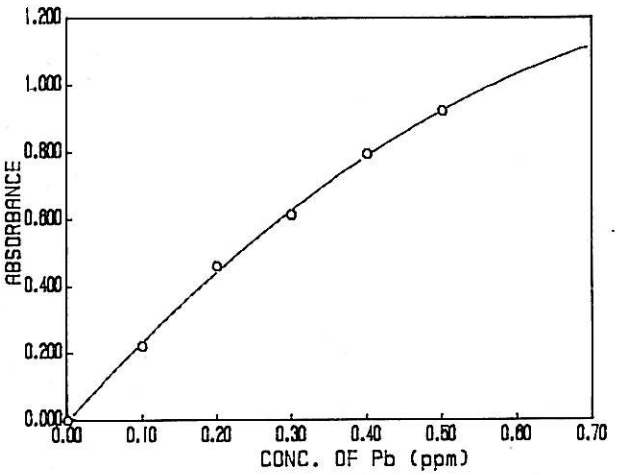



FIG. 1b. Calibration curve for lead.

The characteristic mass for each element at the operation condition stated are shown in Table 3. Results for the determination of Cu, Cr, Fe, Pb, Ni and V in twelve gas oil range fractions of export grade Libyan crudes are shown in Table 4.

These results indicate that the maximum content of copper (0.2230 $\mu g\, g^{-1}$) is found in sample 2B. The chromium content is in the range of 0.0004–0.0427 $\mu g\, g^{-1}$. Iron content is maximum (0.6930 $\mu g\, g^{-1}$) in sample 3B and minimum (0.0200 $\mu g\, g^{-1}$) in sample 6A. Nickel content was found maximum (1.0980 $\mu g\, g^{-1}$) in sample 4B and minimum (0.0590 $\mu g\, g^{-1}$) in sample 4A while sample 5A contains less than detection limit (0.0074 $\mu g\, g^{-1}$). The vanadium content ranges from 0.0400 to 0.1450 $\mu g\, g^{-1}$. Comparing these results with trace metal content in gas oils of other middle east crudes [8] show that Libyan gas oils contain less trace contents.

This study demonstrates that trace elements can be determined with good performance by using dry ashing procedure with the help of p-toluene sulphonic acid as an ashing aid. Acceptable precision and less interference was observed when using aqueous solution as standard for calibration graph. The results obtained in this work would help in studying the presence of some trace elements and their distribution in gas oil fractions.

**Table 3. Working Sensitivities of Different Elements**

| Element | Wave length (nm) | Standard Conc. range ($\mu g\, g^{-1}$) | Sensitivity ($\mu g\, g^{-1}$) |
|---|---|---|---|
| Cr | 357.9 | 0.0200–0.1000 | 0.0008 |
| Fe | 248.3 | 0.1000–0.6000 | 0.0005 |
| Cu | 324.8 | 0.0200–0.1000 | 0.0010 |
| Ni | 232.0 | 0.5000–3.000 | 0.0074 |
| Pb | 217.0 | 0.1000–0.5000 | 0.0021 |
| V | 318.5 | 0.5000–4.0000 | 0.0216 |

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**Table 4. Trace Metal Concentrations in Different Samples**

| Crude Fraction | Temp. Range (°C) | Trace metal content (in $\mu g\, g^{-1}$) Copper (Cu) | Chromium (Cr) | Iron (Fe) | Lead (Pb) | Nickel (Ni) | Vanadium (V) |
|---|---|---|---|---|---|---|---|
| 1A | 220–280 | 0.0219 | 0.0055 | 0.1740 | 1.0520 | 0.2090 | 0.0950 |
| 1B | 280–340 | 0.0052 | 0.0013 | 0.1000 | 0.1637 | 0.1600 | 0.0900 |
| 2A | 220–280 | 0.0639 | 0.0427 | 0.5130 | 0.1570 | 0.3700 | 0.0550 |
| 2B | 280–340 | 0.2230 | 0.0137 | 0.0700 | 0.1720 | 0.1990 | 0.0750 |
| 3A | 220–280 | 0.0052 | 0.0078 | 0.4020 | 0.2700 | 0.1990 | 0.1070 |
| 3B | 280–340 | 0.1390 | 0.0220 | 0.6930 | 0.0107 | 0.8470 | 0.0620 |
| 4A | 220–280 | 0.0453 | 0.0151 | 0.2260 | 0.0870 | 0.0590 | 0.0520 |
| 4B | 280–340 | 0.0059 | 0.0142 | 0.4520 | 0.1009 | 1.0980 | 0.0970 |
| 5A | 220–280 | 0.0260 | 0.0165 | 0.1250 | 0.0848 | 0.0370 | 0.1450 |
| 5B | 280–340 | 0.0052 | 0.0215 | 0.1320 | 0.1880 | 0.1500 | 0.0820 |
| 6A | 220–280 | 0.0379 | 0.0004 | 0.0200 | 0.1210 | 0.0750 | 0.0720 |
| 6B | 280–340 | 0.0052 | 0.0160 | 0.4240 | 0.1980 | 0.1250 | 0.0400 |

Trace metal content (in $\mu g\, g^{-1}$)