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Copper Content in Crude Oil at Kurdistan Region – Iraq

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ABSTRACT

Crude oil samples collected from different places of Kurdistan region (Kirkuk, Kohrmalah 1, Kohrmalah 2, TT-18, TT-14, TT-04, TT-15, TT-07, TT-06 and TT-17) were analyzed for their Copper content. The results showed that concentration of copper are in the order: Kohrmalah 2 > TT-18 > TT-07 > TT-17 > TT-06 > Kohrmalah 1 > TT-15 > TT-14 > TT-04 for crude oil samples. The method was successfully used in the determination of Cu (II) in crude oil as well as in some environmental and industrial waste water. The method has high precision and accuracy.

Keywords: Copper, crude oil, Kurdistan region.

INTRODUCTION

The most important metallic and nonmetallic elements found in the residue crude oil are (S, Ca, Mn, Fe, Co, Ni, V, Pb) with concentration varying as metals ranged between (0.1-1) ppm as (Mo, La, Pb, Ba, Mn, Zr, Sr), metals ranged between (1-10) ppm as (Sn,K,Mg,Al) and metals ranged between (10- 100) ppm as Na, Fe, V, Ni, Ca) [1]. The determination methods of copper in crude oil mainly included atomic emission spectrometry [2], Polarography [3], X- ray fluorescent spectrometry [4] and spectrophotometry [5-7]. The total metal content in crude oils has an extended concentration range, and statistical analysis was the first tool applied to investigate general elemental distribution patterns. The analysis of oils worldwide having different viscosities and asphaltene concentrations showed that the more residual the oil, the higher the metal content. Alkaline and alkaline earth elements are predominantly associated as carbonates and halides with the emulsified water incorporated into the oil during migration and accumulation in the reservoir, but their presence can also be the result of contamination from injected water during secondary oil recovery [8].

The objective of this study is to evaluate the copper content of samples from different places at Kurdistan region – Iraq crude oil.

MATERIALS AND METHODS

All experiments were conducted at the laboratories of oil technology department – Koya technical institute.

Reagents and solutions: Stock solution of EDTA was prepared by dissolving 2 g of analytical grade (≥99%) of disodium dihydrogen ethylenediamine tetraacetate dihydrate in (500mL) de-ionized water. Acids used are HNO_3 (1+3) and HCl (1+5).

Sample preparation: Weigh (10 – 12) g of sample into a crucible. Then carbonize the sample by using conradson carbon residue instrument. The carbonized sample must transfer into a muffle furnace and ashed at 600°C for 3 h. When the ash turned to grayish brown completely, 6 mL of (1+3) HNO_3 was adding to dissolve the oxide at room temperature. The sample was vaporize to near dryness, and then washed with a little water after cooling. The obtained solution was transferred into volumetric flask. Dilute to the scale for use.

Determination of copper: Take 25 mL of above sample to 250 ml conical flask and then add 2 mL of HCl (1+5). The acidity must adjust to 5.5 – 6. Titrate with EDTA standard until the color jumped from mauve to brilliant yellow. The volume of EDTA = V_1ml. 25mL of the sample above transfer into a conical flask, add 5 mL of HCl (1+5) and 1 mL of thiourea solution. Shack for 1 min and add 2-3 drops of Xylenol orange indicator. The pH must be adjusted by HCl (1+5) to 5.5 – 6. This solution was titrated to brilliant yellow with EDTA.

Calculations:

$Cu\ (\mu g\ g^{-1}) = C\ (V_1 - V_2) * M_{Cu} * 10^3\ ms^{-1}$

Where:

C: concentration of EDTA standard (M)

V_1, V_2: Consumed volume of EDTA solution for total metal ions and the metals except for Cu^{+2}, respectively, mL

M_{Cu}: Molar mass of copper, 63.55 g mol^{-1}

ms: Mass of sample, g

RESULTS AND DISCUSSION

Crude oil is an important material for petrochemical industries. Some metals such as copper is usually present in crude oil, it is not only cause in environmental pollution, but also harmful for petrochemical processing, storage and transportation. The presence of copper in crude oil can worsen the selectivity of catalyst, decrease activity and even permanent poisoning and loss activity. Therefore the accurate determination of copper in crude oil and investigation of catalyst poisoning have great significance to the studies on chemical structure of crude oil, mechanism of catalytic reaction and environmental treatment and improvement of product quality [9].

Crude oil is a complex matrix of varying viscosities and mixed phases (organic, water and particulate matter) and therefore not an ideal matrix for analysis. The determination of the metals in crude oil requires pretreatment to the sample before presentation to the instrument. This is the stage where most of the errors occur and is time consuming. The selection of a particular procedure depends upon (1) analytical technique to be employed,(2) nature and the number of the samples to be analyzed, (3) desired degree of precision and accuracy required, (4) availability of the equipment, materials and reagents and (5) the cost of analysis. It is generally desired that analysis is completed within shortest time with minimum contamination, using smallest quantities of the reagents and the samples and little residues and waste generation [10].

Metal determination in crude oil is carried out by using dry ashing, dilution in organic solvents or using micro-emulsions. The use of micro-wave radiation as a potential sample preparation technique has been applied due to high efficiency of heat transfer and sample digestion efficiency. Literature data concerning metal and metalloid determinations in the crude oil by direct sample introduction is also available [11].

Table 1: Copper content (ppm) in different samples from Kurdistan region

No.	Sample	Copper (ppm)
1	Kirkuk	158.875
2	Kohrmalah 1	105.916
3	Kohrmalah 2	799.670
4	TT-18	344.229
5	TT-14	90.029
6	TT-04	42.366
7	TT-15	95.325
8	TT-07	275.383
9	TT-06	169.466
10	TT-17	222.425

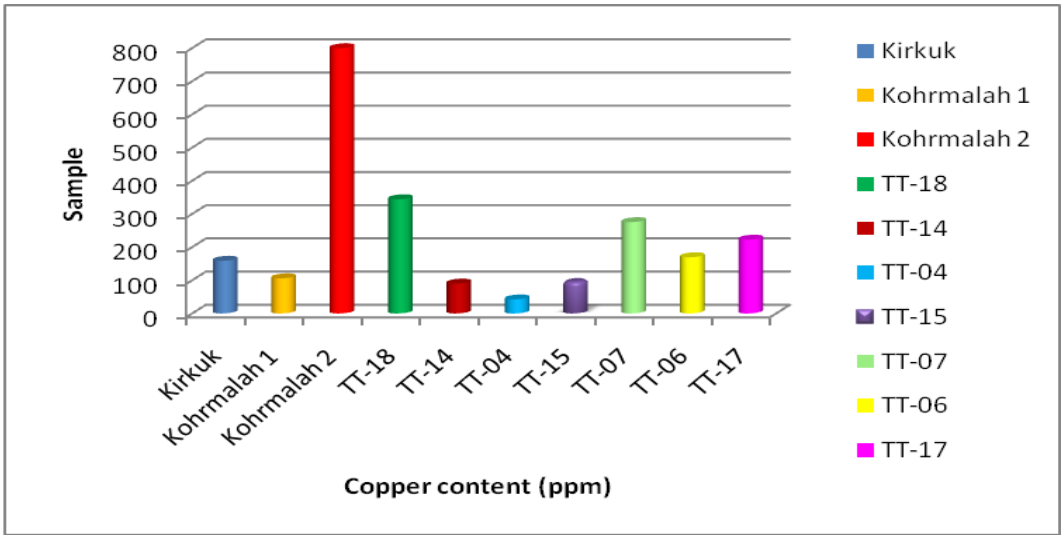

Figure (1): Flow chart of copper content (ppm) in samples

Ashing is used for complete elimination of organic matter, before analytical determination and is based on the ignition of the organic matrix in air or in the stream of oxygen, followed by the dissolution of the residue in an acid medium. This is one of the cheapest sample preparation procedures. Larger quantities of the sample could be used and the analyte could be concentrated into small volume of dilute mineral acid (HCl or HNO_3).

This also makes possible the use of aqueous standards for the calibration of equipment. The main disadvantages of the dry ashing procedure for crude oils are the risks of contamination or loss of the analyte due to the formation of volatile compounds.

The results of our work were listed in table and (1) figure (1).

APPLICATIONS

This method is very important for any petroleum unit, where, the copper content has direct effect on protecting the activity of catalyst, protecting refinery plants, pipelines and tanks away from corrosion, also, copper is an environmental pollutant, then, solutions must be applied to protect environment. In addition, copper in trace amounts is important industrially**,** as a toxicant and as an occupational hazard.

CONCLUSIONS

The findings of this study show the copper content in different samples of crude oil from different places at Kurdistan region – Iraq.

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