



Determination and Removing of Mercury from Heavy Crude Oil by Extraction with Aqueous solutions

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Abstract:

Mercury can have significant impact on petroleum and related industries, it is also known to poison catalysts used in refining processes. Wet ash methods was widely used in determination of mercury in crude oil but the elemental and organic mercury are volatile and losses are also expected. An investigation of the use of Aqueous solution to prevent loss of mercury during wet digestion resulted in consistently good recoveries from crude oil samples. In this research diluted aqueous solution of sodium polysulfide is used and the parameters studied are polysulfide aqueous solution concentration, time, and ratio of the aqueous solution to crude oil, and will take different forms of heavy crude oil from several fields and the previous measurement of mercury both ways (wet ash) and new (aqueous) and compare the results. The results show that the procedure is reproducible and comparable in accuracy to other establish procedures.

Keywords: mercury, crude oil, ashing process.

تعيين وإزالة الزئبق من النفط الخام الثقيل باستخدام الاستخلاص بالمحلول المائي

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الخلاصة :

يعتبر الزئبق من العناصر التي لها تأثير ملحوظ على النفط الخام والصناعات النفطية، كما ويعتبر مسمما للعوامل المساعدة المستخدمة في العمليات النفطية، وتقيم النقط على نسبة احتوائها للزئبق وقد استخدمت الطرق المعروفة بالترميز لتعيين الزئبق في النفط الخام وظهرت هذه الطرق مساوية تكمن في السمية الناتجة من تبخر الزئبق اثناء عملية الترميد اضافة الى الاخطاء الحاصلة في القياس بسبب فقدان . حيث تم استخدام محلول مائي لاستخلاص الزئبق من النفط الخام ثم قياسه وهو في محلوله المائي . وتم استخدام المحلول المخفف المائي للبولي ثايو سلفاد الصوديوم وتم دراسة المتغيرات تركيز محلول الثايو سلفاد وزمن الخلط والنسبة بين حجم المحلول المائي للنفط الخام تم اخذ نماذج مختلفة من النفط الخام الثقيل من عدة حقول و قياس الزئبق بالطريقتين السابقة (الترميز) والجديدة (المحلول المائي) ومقارنة النتائج . حيث اثبتت النتائج ان الطريقة الحالية اكثر دقة واسرع من طريقة الترميد المتبعة .

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Introduction

Mercury and other trace metals/metalloids in hydrocarbons can have significant impact on petroleum and related industries. On top of regulatory concerns, trace metals in crude can effect process equipment; mercury can amalgamate with aluminum to create a more brittle alloy, which has been associated with structural failures(The Courier-Mail,2004). Trace metals/metalloids in crude oil can have significant environmental impact in wastewater, solid waste, or emissions that may have concentrations above regulated levels. They can also accumulate in equipment, causing health and safety concerns during operation and maintenance (Liang *et al.*,2004). Crude oil containing high levels of mercury and other trace metals are typically discounted at significant cost per barrel(US EPA,2001). This problem is compounded as determination of low-level metals concentrations in hydrocarbons has been historically inaccurate, with insufficiently low detection limits. These limitations can often be directly associated with the difficulty to fully decompose the matrix. There is a need to determine the trace metals in the crude oils quantitatively because of their importance in the geochemical characterization of its source and origin. Trace metals have been used as a tool to understand the depositional environments and source rock(Alberdi-Genolet and M.Tocco; R; 1999). The determination of metal ions in crude oils has environmental and industrial importance. The metal ions like vanadium, nickel, copper and iron, behave as catalyst poisons during catalytic cracking process in refining of crude oil.The metal ions are released in the environment during exploration, production and refining of crude oil.The determination of mercury content in crude oil is also important for petroleum industry, because the metal can deposit in the equipment, which could affect the maintenance and operation (Wilhelm *et al.*,2006). It is therefore considered necessary to know the concentration of metals in the oils for meaningful impact assessment.

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 [Oliveira, E., 2003]. 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 (Amorin *et al.*,2007).

Metal determination in crude oil is carried out by using dry ashing, dilution in organic solvents (Annual Book of ASTM,2000, Annual Book of ASTM 2002) or using micro-emulsions (Santella *et al.*,2008). Dry 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 procedure. Larger quantities of the sample could be used and the analyte could be concentrated into small volume of dilute mineral acid (HCl or HNO₃). This also make 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(Ekanem *et al.*,1998).

In this method for removing mercury from a mercury-contaminated crude oil comprising contacting it with an aqueous dilute solution of alkali metal sulfide salts and separating a liquid hydrocarbon phase substantially free of mercury from said mixture of mercury-contaminated liquid hydrocarbon and aqueous dilute alkali metal sulfide solution for avoiding losses of Hg by volatilization during ashing.

Materials And Methods

Samples of crude oil is cared out from several Iraqi oil fields. The chemicals used were: Sodium hydroxide; sodium sulfide nonahydrate (Na₂S•9H₂O);sulfur, nitric acid wer purchased from Aldrich Chemical Co. The chemicals used in this study were mostly reagent or higher grades and used as received without further treatment.

Instrumentation

Mercury was analyzed following a regulatory-approved, modified version of US EPA Method 1631 using a RA-3000A Mercury Analyzer from Nippon Instruments cold vapor atomic fluorescence spectroscopy (CV-AFS).Separating funnel with dimensions 30cm height and 5cm width.

Experimental Methods:

A- Aqueous Solution Method

Preparation of Dilute Aqueous Solution

- 1 dissolve 480 g of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in 500 ml D.W and heating Near boiling .
- 2 Adding 40 g of NaOH and 18g of Sulfur
- 3 stirred vigorously and complete the volume to 1000 ml with D.W. ,Preferably the solutions are made up of such compounds as sodium or potassium bisulfide, sulfide, or polysulfide and contains such ions as $\text{HS}^{\text{sup.-}}$, $\text{S}^{\text{sub.2.sup.=}}$ and $\text{S}^{\text{sub.X.sup.=}}$ and their mixtures to levels of 1 to 50,000 ppm, but preferably 10 to 5,000 ppm. The pH of the solutions is controlled to a range of 7 to 12 with an alkali such as NaOH.

B- Ashing Method

- 1 25 ml of crude oil heating in ceramic crucible .
- 2 Adding nitric acide to crucible after cooling and leave it for one hour ,and then heat for medium heating with continuous stirring for one hour.
- 3 Cooling and add deionized water and diluted to 50ml.
- 4 Determine the mercury in sample by mercury analyzer.

Removing of Mercury

Twenty-five (25-) cc portions of condensate were mixed with measured volumes of Na_2S_x and NaOH aqueous solutions of varied concentrations. The mixtures were mechanically homogenized with a blender, and after each had been allowed to settle for 5 to 15 minutes, the resulting oil and aqueous phases were separated. The oil phase from each run was analyzed for water, sulfur and mercury content. The test results suggest that the most important process variables in removing mercury from the condensate are intensity of mixing, concentration of Na_2S_x , volume ratio of Na_2S_x solution of caustic, and efficiency of phase separation. Figure-1 is a plot showing the removing of mercury by extraction with aqueous solutions. The samples well determination by RA-3000A Mercury Analyzer from Nippon Instruments to measure the mercury concentration. [1-11]

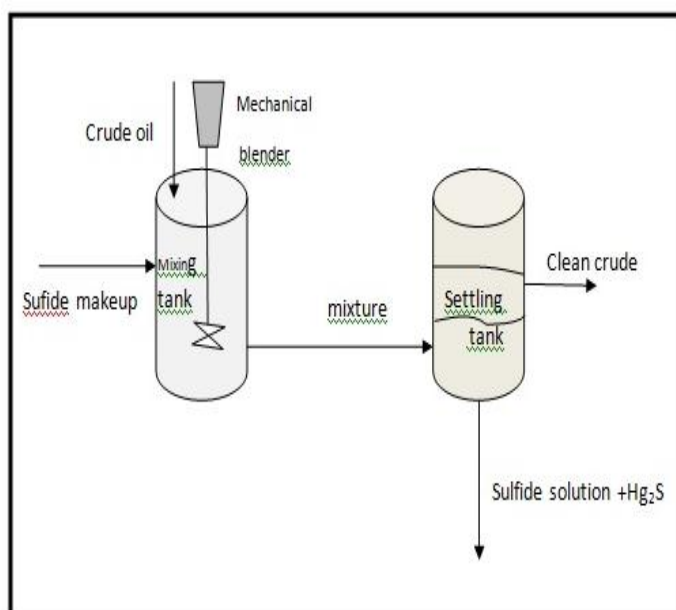


Figure 1- Removing Of Mercury by Extraction with Aqueous Solutions

Results and Discussion

1- Effect of Mixing Time:

effect of mixing time has been studied for time interval of 1 to 10 minutes with other optimum conditions. It was observed in figure-1 that initially removing efficiency increases with time and after 6 minutes it remains steady indicating complete removing of mercury. Therefore 6 minutes time was considered as optimum time to ensure complete removing of mercury. The figure-2 shows the result of mixing time .

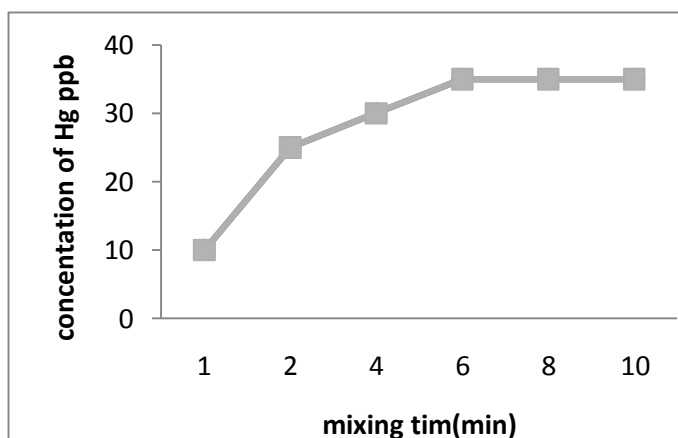


Figure 2-The Effect of Mixing Time On the Removal of Mercury from Crude Oil.

2- Effect of Concentration of Sodium polysulfide

Figure-3 shows the effect of sodium polysulfide concentration in the range 200-1500ppm as a function of time from 6 minutes on the removing efficiency of mercury maintained at liquid /liquid ratio 2:1 . The sodium polysulfide concentration decreases result clearly suggest that maximum removing of mercury is attained with about 1000ppm of sodium polysulfide concentration and further decrease of sodium polysulfide concentration had marginal effect on removing of mercury.

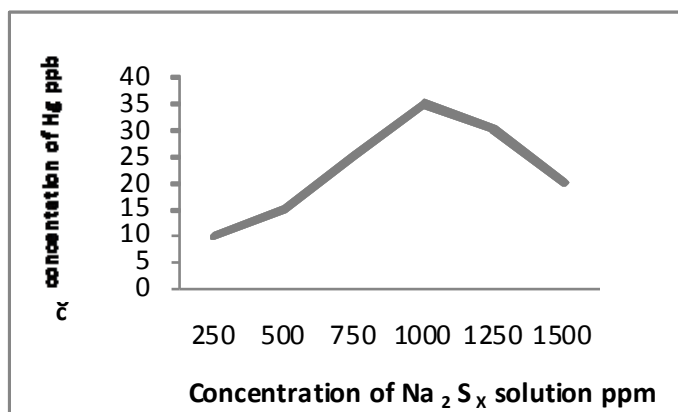


Figure 3- the Effect of Sodium polysulfide Concentration on Mercury Removal.

3-Effect of Volume Ratio

Experiments were carried out at 0.5:1 to 2.5:1 ratio of volume of aqueous polysulfide solution to volume of crude oil. The results clearly suggest that the optimum ratio of volume of aqueous polysulfide solution to volume of crude oil is 2:1.figure-4 is a plot showing the effect of the ratio of volume of aqueous polysulfide solution to volume of crude oil.

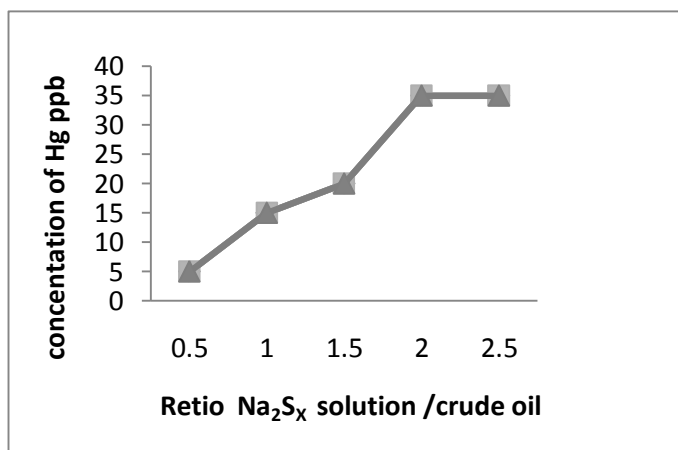


Figure 4- The Effect of The Ratio of Volume of Aqueous Polysulfide Solution to Volume of Crude Oil.

5- Compared the Extraction Method with Ashing Method

Figure-5 is a plot showing the compared between extraction with aqueous polysulfide solution to ashing method to determination of mercury concentration .The results show that determination of mercury with use of aqueous polysulfide solution method more accuracy than using ashing method.

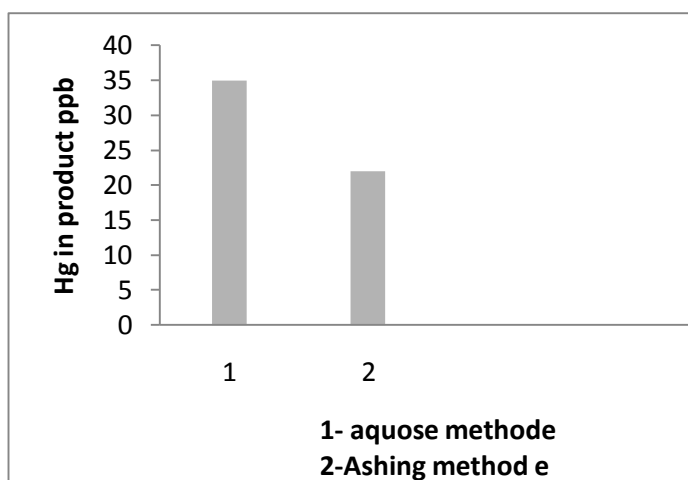


Figure 5- The Compared between Extraction with Aqueous polysulfide solution Method to Ashing method.

Conclusions:

The results showing that the best time for mixing is 6 mint and the best concentration of sodium polysulfide is 1000ppm with ratio of volume of sodium polysulfide to volume of crude oil 2:1 ,as well as this method is proved the avoid of loss of the analyte due to the formation of volatile compounds through ashing method

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