

# EVALUATION THE PRECISION OF "DOCTORE TEST" FOR MERCAPTANS DETECTION IN PETROLEUM PRODUCTS BY SULPHIDE ION-SELECTIVE ELECTRODE



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## ABSTRACT

Mercaptan sulphur in petroleum products ( Motor fuel, kerosene, aviation fuel,...etc) were detected with standard test method of British Institute of Petroleum ( IP) that marked by the number IP-30 . The detection of this method was qualitatively and the precision has not been established. In this research a précised results were tabulated for the IP-30 test method, using sulphide ion selective electrode. A comparable results of quantitative value for mercaptans of IP-30 test method now are available.

## INTRODUCTION

Sulphide ion-selective electrode has been applied in monitoring sulphide in industrial liquors(1), waters(2-4), atmosphere (5),soil and sediments (6). It was also used for following bacterial growth (7-8) and for determining low sulphide levels in biochemical systems (9), in tooth past abrasive (10) and blood(11). The electrode also used for determining mercaptans in petroleum products (12).

A method designated as British institute of petroleum (IP-30)(13), which corresponded to that of American Standard Test Method (ASTM-D484-52)(14) was intended for the detection of mercaptans sulphur in motor fuel, kerosene and similar petroleum products.

The results of testing in this method are reported as negative, slightly positive and positive depending on the discoloration of sulphur floating at oil-water interface or by discoloration of either of the phase as a result of shaking of the mixture of the sample with sodium plumbite solution and flower sulphur(Table.1).

The precision of this method has not been established, so in this research, an evaluation has been done using Sulphide ion-selective electrode. The British institute of petroleum methods (IP-30) will be then suitable for setting specifications on petroleum products as a quality control tool.

## EXPERIMENTALS:

A series of standards samples of n- butyl mercaptan ( 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0,7.0,8.0, 9.0,10.0, 20.,30.,40.,50., 75. and 100 ppm ) were prepared using kerosene ( free of mercaptan) as a diluent .

These standard solutions were checked for mercaptane sulphure using the potentiometric methods. The sample was dissolved in 100 mls of titration solvent and then titrated against alcoholic 0.1N silver nitrate; the end point was checked by Sulphide ion-selective electrode.

Each standard sample was checked for mercaptan sulphur presence by (IP-30) test methods. Fresh untreated petroleum products were examined by the potentiometric mode and the (IP-30) test methods for comparison.

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## RESULTS AND DISCUSSION

In the past few years a large numbers of researches have been done in the field of ion-selective electrodes, the development and various applications of new electrochemical sensors continue to be a rapidly growing area of analytical chemistry.

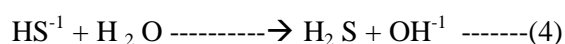
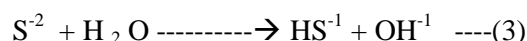
Sulphid ion- selective electrode is sensitive and capable of measuring very low levels of Ag<sup>+</sup> and S<sup>2-</sup>. The electrode responds either directly to silver ions or indirectly to sulphid ions. When it is used as a sensor for silver ions, its potential follows the Nernst equation .

$$E = E_0 + 2.303 (RT/ ZF) \text{Log a Ag}^+ \text{ -----(1)}$$

When it is used as a sensor for sulphid ions, its potential follows the Nernst equation.

$$E = E_0 - 2.303 (RT/ ZF) \text{Log a S}^{2-} \text{ -----(2)}$$

Because of the appreciable hydrolysis of the sulphid ion according to equations (3,4) of which only equations (3) affects the sulphid ion concentration in alkaline solution:



The total concentration of the dissolved sulphid is the sum of the concentration of the three species of sulphid.

$$[\text{S}^{2-}]_{\text{total}} = [\text{S}^{2-}] + [\text{HS}^{-1}] + [\text{H}_2\text{S}] \text{ -----(5)}$$

Thus, the sulphid measurements are difficult, since it is subjected to protonation by hydrogen ions and also it is subjected to loss by volatilization, At pH { = < 4}, the sulphid is almost exclusively present as dissolved hydrogen sulphid gas [ H<sub>2</sub>S ], at pH { => 4} the hydrogen sulphid progressively dissociates to form bisulphid ions [ HS<sup>-1</sup> ], at pH { = 7}, the solution contains equal proportions of [ HS<sup>-1</sup> ] and [ H<sub>2</sub>S ]. between pH {= 9—10} the dissolved sulphid would be almost exclusively present as hydrogen sulphid ions [ HS<sup>-1</sup> ]. If the pH raised

again, hydrogen sulphid ions dissociates to form divalent sulphid ions [ S<sup>2-</sup> ] which will be predominate at pH { => 13}.

To overcome the protonation phenomena during measurements, sulphid samples and standards were buffered and the determination of sulphid at pH { => 13} is practically useful and was recommended by Orion Research Inc. ( 15 )

In this research, buffer titration solvent was used from Isopropanole and 1% aqueous ammonium hydroxide following the USA method (UOP-163) (12 )

The sulphid samples were stored under purified nitrogen atmosphere to overcome the oxidation phenomena of sulphid ion by dissolved oxygen to sulphite, thiosulphate and sulphate.(16)

The prepared standard mercaptan samples that checked by sulphide ion- selective electrode showed that

The standard mercaptan concentrations of 0.5 to 2.5 ppm gavenegative results with (IP-30) test method.

Standard mercaptan concentrations of 2.75 to 5 ppm showed slightly positive results with (IP-30) test method.

Standard mercaptan concentrations with (6) ppm mercaptan and above(Table 2), showed a positive results of (IP-30) test method.

To evaluate the work, fresh sample of kerosene hydro treating unit and untreated kerosene from storage tanks were checked. The negative result of (IP-30) was of 2.0 ppm mercaptan sulphur with sulphide ion-selective electrode for kerosene from the unit.

A slightly positive results of (IP-30) was of 5 ppm mercaptane sulphur with sulphide ion-selective electrode for kerosene from storage tanks.

Now it can be concluded that if a sample was tested for mercaptane sulphur with (IP-30), so, its roughly results can be estimated as a quantitative results giving fast and accurate mercaptan sulphur concentration (Table -3).

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**Table (1) The British institute of petroleum methods (IP-30) report**

Discoloration of sulphur of either phase	Sulphur
None	Negative
Slight	Slightly positive
Definite	positive

**Table (2) The expression of British institute of petroleum method (IP-30) by the potentiometric mode of sulphide ion selective electrode method**

Potentiometric mode with sulphide ISE	(IP-30)
0.5- 2.5 ppm mercaptan sulphur	Negative
0.5- 5.0 ppm mercaptan sulphur	Slightly positive
> 5.0 ppm mercaptan sulphur	positive

No Discoloration of sulphur of either phase	< 2.5 ppm
Slight Discoloration of sulphur of either phase	2.5- 5.0 ppm
Definite Discoloration of sulphur of either phase	> 5.0 ppm

Table (3) The final modified British institute of petroleum method (IP-30) report

The (IP-30) test results	Modified report of mercaptane sulphure
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## تقييم طريقة (فحص الدكتور) لتقدير المركبات في المنتجات النفطية باستعمال قطب الكبريتيد الانتقائي.

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الخلاصة:

تعد طريقة "فحص الدكتور" المعروفة بطريقة المعهد البريطاني للنفط (IP-30) والمطابقة لطريقة القياسي الأمريكي للفحص والمواد (ASTM- D484-52) مقياساً تحليلياً نوعياً سريعاً للكشف عن تواجد بعض مركبات الكبريت المهمة في المنتجات النفطية وخاصة المركبتان RSH . تم في هذا البحث توسيع مدى الفائدة من استخدام هذه الطريقة وتحويلها من طريقة تحليلية نوعية إلى طريقة تحليلية كمية، باستخدام قطب الكبريتيد الانتقائي لتقدير المركبتان في نماذج منتجات نفطية أعطت كشفاً تحليلياً نوعياً عن المركبتان. لقد تم مطابقة قيم المركبتان التي تعطي كشفاً موجبة أو سالبة مع تراكيز محسوبة من المركبتان باستخدام قطب الكبريتيد الانتقائي، لذا يمكن اعتبار طريقة فحص الدكتور طريقة تحليلية كمية سريعة لتعيين المركبتان في مختبرات السيطرة النوعية في مصافي النفط.