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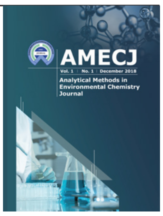

Determination of H_2S in crude oil via a rapid, reliable and sensitive method

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ABSTRACT

Determination of hydrogen sulfide (H_2S) in crude oil is very important due to the environmental impacts, industrial problems, and legal international limitation of transportation. In the present work, H_2S of crude oil is determined by liquid-liquid extraction followed by potentiometric titration. Moreover, three factors including dilution ratio of crude oil with toluene, extraction time of H_2S into the caustic phase and API of crude oil were investigated via factorial design. The ANOVA results have revealed that the dilution ratio, crude type, and extraction time have the highest effect of the recovery of H_2S from crude oil. In addition, the linear dynamic range of the method was from 1 up to 2000 ppm which can be manipulated for lower or higher concentration by further optimization of the above-mentioned parameters. Finally, this method is rapid, reliable, operator-independent, which these characteristics make it a useful technique for the field test of crude oil and overcome extreme uncertainty of H_2S measurement.

1. Introduction

H_2S is one of the most hazardous compounds which is colorless gas and can dissolved in aqueous and organic solvents. In addition, it is a poisonous and corrosive compound. In addition, it causes environmental damages [1-3]. H_2S can be present in petroleum and petroleum products including asphalt, residual fuel oil, mid-distillates and their blend, natural gas and LPG [4-6]. H_2S is evolved and produced in production of fossil fuels in oil and gas industry. There is very tight international regulations in the transportation of crude oil and hydrocarbons [7]. Due to this regulations, determination of H_2S at low level and also high level is very critical from industrial and environmental point of view [8, 9]. There are many methods for the determination of H_2S in crude oil and its derivatives. The method of measurements is given in Table 1. As can be seen, there is no a valid and standard method for the determination of H_2S in crude oil

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specially in the presence of mercaptan, chlorine and some basic additives and scavengers [10-17]. Furthermore, there is demand for a method which comprises requirements of a good method. These requirements including easy operation in field or laboratory, low health and safety problem, operator independent, low cost, repeatable, reproducible and providing very low detection limit as well as wide linear dynamic range. Among the methods of H_2S determination, each of them has its own limitation [18-20]. The health and safety hazards related to H_2S are summarized in Table 2 [21]. Furthermore, among the properties of the crude oil reported for the sale and refinery designing, H_2S may be the most unstable parameter, even in comparison with Reid vapor pressure and specific gravity. So far, to the best of our knowledge, there is not an appropriate analytical method for determination of H_2S in crude oil for use in both oil field and laboratory test. In the present work, a rapid method was developed and investigated using factorial experimental design for the determination of H_2S of crude oil which can be used in laboratory or field test and led to the repeatable and accurate results.

2. Materials and Methods

All chemicals were purchased from Merck and used as received. In a typical determination, 50 mL of crude oil and predetermined amount of toluene as Diluting ratio were poured into a decanting funnel and shaken for a about 5 minutes. Then 25 mL of 5 w/w% aqueous caustic solution was used as extracting agent and was shaken for a predetermined time. The mixture was aged for 10 minutes to separate oil and aqueous solution. Afterwards, 10 mL of aqueous solution was decanted on a paper filter, and the filtrate was collected in a titration beaker. After addition of 2 mL on concentrated solution of ammonia, the filtrate was titrated with 0.05 N of silver nitrate solution. The first equivalent point at about -600 mV is related to the H_2S. Titration was carried out

Table 1. Standard methods of H_2S determination and their properties (Nadkarni 2000).

Method	Disadvantage	Scope of work	Dynamic range
ASTM D5623	Narrow dynamic range, High cost, Limited sample boiling range	GC of Liquid distillates with FBP < 230 °C	0.1 - 100 ppm
UOP 212	Limited sample boiling range, High cost	Potentiometric titration, ethane to such gasoline	1 to several thousand ppmw of H_2S
ASTM D5705	Only applicable to vapor phase, Poor repeatability	H_2S in the vapor phase (equilibrium) of a residual fuel oil for field test using gas detection tubes and Can test	5 ppm v/v to 4000 ppm v/v
UOP 163	Not applicable to crude oil, Complex data interpretation	H_2S in Liquid hydrocarbons by potentiometric titration	1 up to 100 ppmw.
ASTM D7621 IP 570 ISO 8217	Not applicable to crude oil, mercaptan interference	H2S in Fuel Oils by Rapid Liquid Phase Extraction	1 up to 50 ppmw
UOP 41 ASTM D4952 Doctor Test	Only for qualitative analysis, Using of poisonous metal	qualitative test of H2S in gasoline, jet fuel, kerosine and similar petroleum products and solvents	
ASTM 6021	skilled operator and complex calculations, High cost	H2S in Residual Fuels by Multiple Headspace Extraction and Sulfur Specific Detection	0.01 to 100 ppmw
IP 399	Complex procedure and pure materials needed. Oxidation and absorption may occur.	H_2S in Residual Fuels by sprctrophotometric determination.	0.50 to 32 ppmw

Table 2. Exposure limit and its related hazards.

Concentration mg/kg	Health & Hazard Effect
< 0.02	Odor Detection Limit
10	8 Hours Exposure Limit
15	15 Min. STEL
100	Common Ship Headspace Spec.
300	Considered Immediately Hazardous
713	LC50 Concentration
1000	Common Tank, Ship Headspace Concentration

using a Metrohm titrando 880 according to the UOP 209.

For the optimization of the condition of determination, a factorial design was applied for the investigation of three main effects, including time required for extraction, diluting ratio ration and crude type according to its API. 12 experimental runs were designed and carried out. Calculation and modeling of results were done using Design Expert 7.

Recovery is defined as the ratio of the concentration of the H_2S obtained in the designed test to H_2S obtained at 2 hours and 60 C with diluting ratio of 5.

3. Results and Discussion

The condition of statistically designed runs and their corresponding results are given in Table 3.

Analysis of variance of obtained results is calculated and give in Table 4. The obtained Equation for model is given as Eq. 1 in terms of coded factors.

Recovery = +91.75 - (1.25 * A[1]) + (0.50 * A[2]) +(4.75 * B) + (1.75 * C) + (0.42 * BC) (Eqn. 1)

As seen in Figure 1, and according to the Equation 1 and ANOVA (Table 4), it can be said that Time has very little effect on the recovery of H_2S. It is a very good property for an analytical method to carry out in short time.

Figure 2 displays the effect of Diluting ratio which is the most effective factor among all. Moreover, it is generally known that crude oil has very broad range of properties in term of density and viscosity. H_2S is trapped in the complex matrix

Table 3. Designed test runs for H_2S determination.

Std. run order	A: Time (min)	B: Diluting ratio	C: Crude type (API)	Recovery %
1	2	1	22	84
2	6	1	22	86
3	10	1	22	87
4	2	2	22	93
5	6	2	22	95
6	10	2	22	95
7	2	1	36	87
8	6	1	36	89
9	10	1	36	89
10	2	2	36	98
11	6	2	36	99
12	10	2	36	99

Table 4. ANOVA of obtained results of H_2S analysis.

Source	Sum of Squares	df	Mean Square	F Value	P-value Prob > F
Model	319.1	5	63.8	328.2	< 0.0001
A-Time	9.5	2	4.8	24.4	0.0013
B-Diluting ratio	270.8	1	270.8	1392.4	< 0.0001
C-Crude type	36.8	1	36.8	189.0	< 0.0001
BC	2.1	1	2.1	10.7	0.0170
Residual	1.2	6	0.2	-	-
Corr. Total	320.3	11	-	-	-

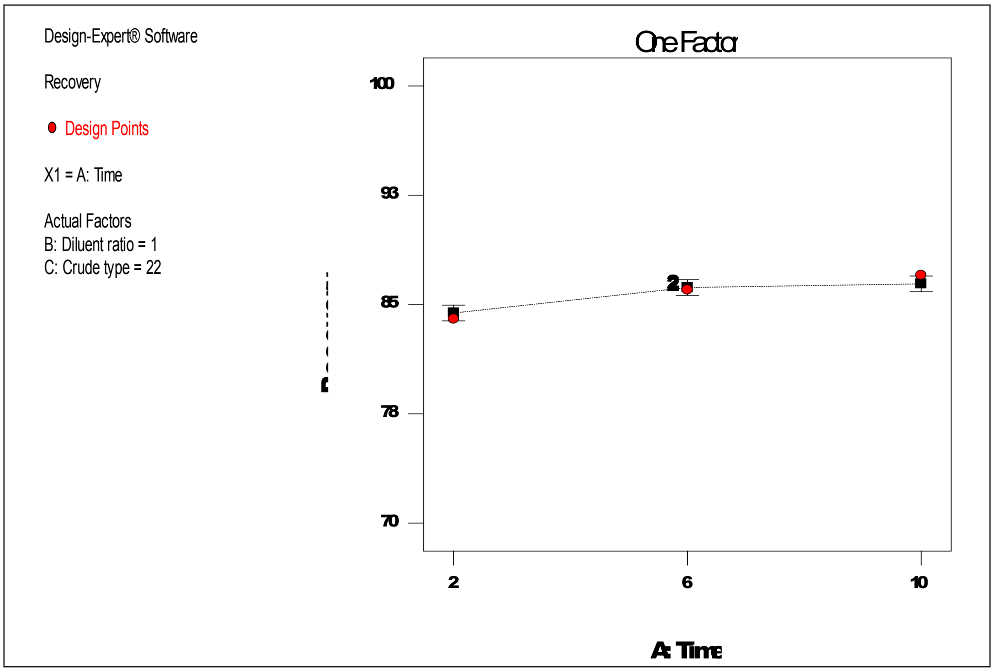

Fig. 1. Effect of factor A: Time on recovery.

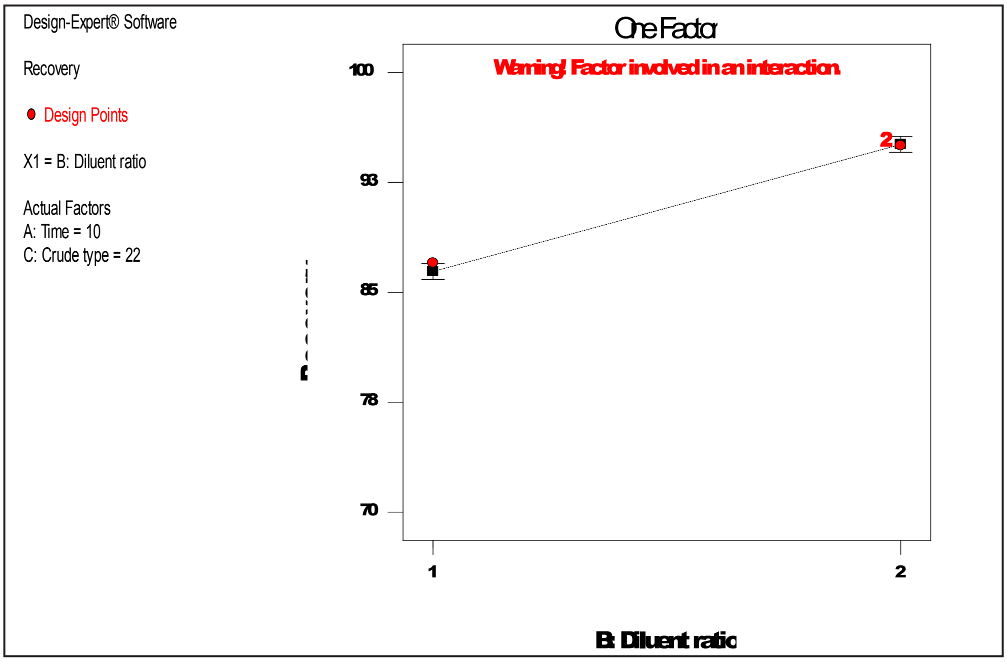

Fig. 2. Effect of factor B: Diluting ratio on recovery.

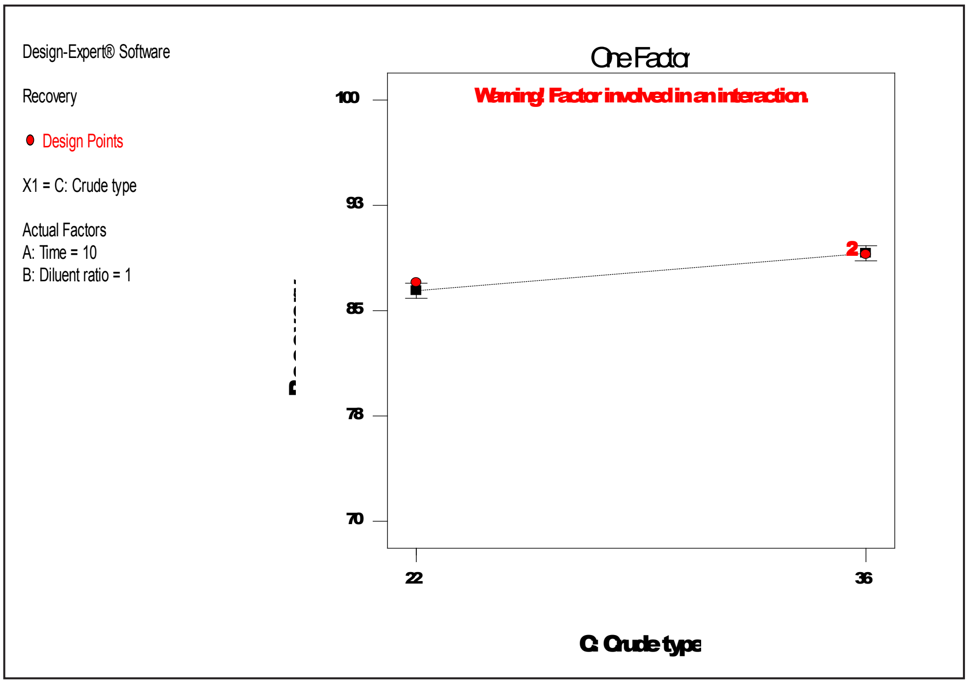

Fig. 3. Effect of factor C:Crude type on recovery.

of crude oil. Thus, the presence of toluene is essential for the dilution of the crude oil and breaks its complex matrix and semi ordered array of large molecules (wax, resin, and asphaltene) to easily evolve the trapped H_2S.

As the crude oil becomes heavier as well as viscose, the evolve of H_2S becomes more difficult and led to the reduction of recovery. So higher Diluting ratio is necessary in case of heavy crude oil. This means that Diluting ratio is the most important factor, as could be deduced from its F value in Table 4.

Figure 3 shows the effect of crude type on the recovery of H_2S. As the API of crude oil increases, the crude oil become lighter and recovery is higher due to the better contact of oil phase and caustic phase an so need to low Diluting ratio and vice versa.

Figure 4 illustrates the interaction of the crude type and diluting ratio in a 3D curve. In case of heavier crude oil, i.e. at lower API, the effect of diluting ratio is very large while at higher API, this effect is lower.

It can overall said that higher diluting ratio and lower extraction time are in favor of recovery despite the fact that higher time, 10 minutes, is steel low for a typical analytical method. For the determination of other merits of this analytical method, additional test was done. In addition, one of the most important properties of a robust analytical methods is Linear Dynamic Range. Four crude oils containing H_2S concentration ranged from 0.2 to 1902 ppmw were examined. Moreover, obtained results showed that any concentration of H_2S can be determined by manipulation of amount of aliquot of crude oil used for test. For the Crude oil contains 1902 ppmw, only 2 grams of crude oil is adequate while for sample containing 0.2 ppmw of H_2S, 100 grams of crude oil is needed. RSD for the 148 ppmw H_2S, in four determinations, was obtained 98%.

Another advantage of this methods is its compatibility for field determination because H_2S is very volatile and unstable. It is generally known

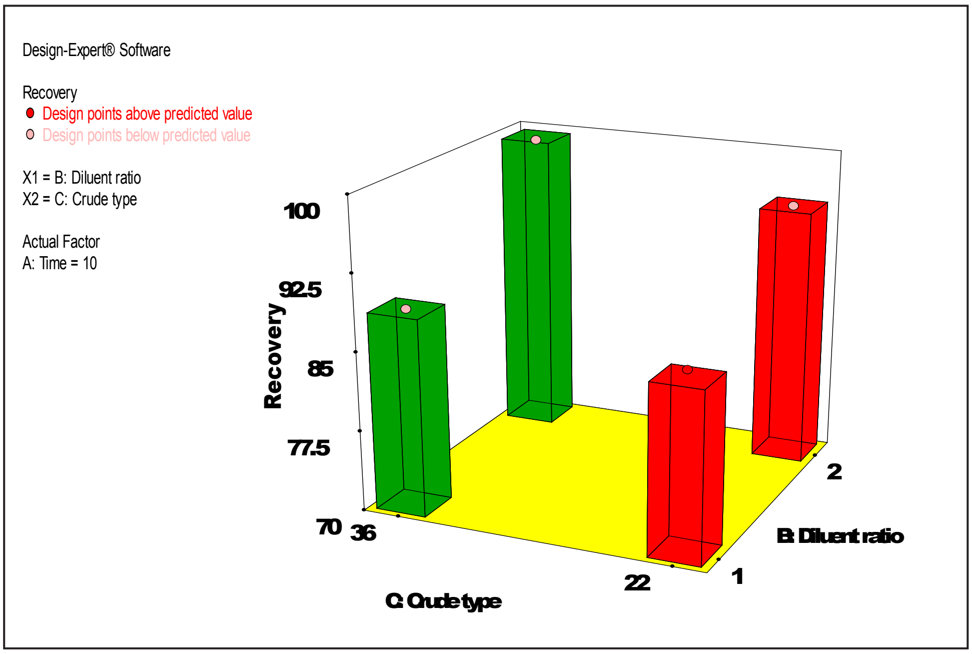

Fig. 4. 2D representation of interaction of Crude type and Diluting ratio.

that long delay between sampling and determination led to the loss of H_2S and cusses lower result.

Furthermore, for field test, operator can pour the fresh crude sample into the decanter containing toluene and caustic solution. After that, vigorous stirring of this mixture led to the absorption of H_2S into the caustic phase and prevent loss of the analyte before titration or transport to laboratory.

It is noteworthy to say that for further improvement of quantification limit and RSD of method, once can increase the absolute amount of crude oil and extraction time. Furthermore, decreasing the amount of caustic solution, which results in higher concentration factor, and using centrifuge instead of decanter for separation of caustic phase prior to titration can improve quantification limit and RSD.

It is well known for those who work in petroleum laboratories that H_2S is very unstable and as the time between sampling and analysis increases, the error of the obtained results drastically increases. In this method, once can pour known quantity of caustic solution in to the pre-weighed sample container and then rinse the crude oil from sampling point in to the container to absorb H_2S into the caustic solution during transfer to the laboratory.

4. Conclusions

In this work, a method comprising the merits of very good analytical method is reported. The method is rapid because the time needed for extraction is lower than 10 minutes and a traditional potentiometric titration. Quantification limit of the method is low enough. Linear Dynamic Range of the method is very broad and this range can be tuned by changing the amount of crude oil. In addition, RSD of the method is up to 98% which is very good for a volatile and unstable compound, i.e. H_2S in a complex matrix of crude oil. The equipment needed for this method is very simple, accessible and cheap. Finally, the procedure of determination, including extraction and titration, is very traditional and don’t need high level of expertise and skill. Furthermore, the method is capable of performing for field test which is very important from industrial point of view. Also, main factors of the method can be tuned easily according to the properties of the crude oil to manipulate lower and upper limit of quantification.

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6. References

[1] R.J. Dieffenstein, W.C. Hulbert, S.H. Roth, Toxicology of Hydrogen Sulfide, Annu. Rev. Pharmacol. Toxicol., 32 (1992) 109-134.

[2] H. Kimura, Metabolic turnover of hydrogen sulfide, Front Physiol., 3 (2012) 1-3

[3] H.S. Kalal, A.A.M. Beigi, M. Farazmand, Determination of trace elemental sulfur and hydrogen sulfide in petroleum and its distillates by preliminary extraction with voltammetric detection, Analyst, 125 (2000) 903-908.

[4] L. Zhang, P. De Schryver, B. De Gusseme, Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: A review, Water Res., 42 (2008) 1-12.

[5] M. Abdouss, N. Hazrati, A.A. Miran Beigi, Effect of the structure of the support and the aminosilane type o the adsorption of H2S from model gas, RSC Adv., 4 (2014) 6337-6345.

[6] N. Hazrati, M. Abdouss, A. Vahid, Removal of H2S from crude oil via stripping followed by adsorption using ZnO/MCM-41 and optimization of parameters, Int. J. Environ. Sci.Technol., 11 (2014) 997-1006.

[7] X. Zhao, J.B. Gao, W.D. Zhang, B. Wang, Study on the risk of a crude oil shipping channel in China, ICCTP, 6 (2011) 3877- 3886.

[8] J. Blomberg, P. Schoenmakers, U.A.T. Brinkman, Gas chromatographic methods for oil analysis, J. Chromatogr. A, 972 (2002) 137-173.

[9]N.E. Heshka, D.B. Hager, A multidimensional gas chromatography method for the analysis of hydrogen sulfide in crude oil and crude oil headspace, J. Sep. Sci, 37 (2014) 3649-3655.

[10] H. Sid Kalal, A.A. Miran Beigi, M. Farazmand, S.A. Tash, Determination of trace elemental sulfur and hydrogen sulfide in petroleum and its distillates by preliminary extraction with voltammetric detection, Analyst, 125 (2000) 903-908.

[11] N.S. Lawrence, R.P. Deo, J. Wang, Electrochemical determination of hydrogen sulfide at carbon nanotube modified electrodes, Anal. Chim. Acta, 517 (2004) 131–137.

[12] S.K. Pandey, K.H. Kim, K.T. Tang , A review of sensor-based methods for monitoring hydrogen sulfide, TrAC - Trends Anal. Chem, 32 (2012) 87–99.

[13] Y. Zhao, T.D. Biggs, M. Xian, Hydrogen sulfide (H2S) releasing agents: chemistry and biological applications, Chem. Commun., 50 (2014) 11788-11805.

[14] J.F.S. Petruci, A. Wilk, A.A. Cardoso, B. Mizaikoff, Online analysis of H2S and SO2 via advanced mid-infrared gas sensors, Anal. Chem., 87 (2015) 9605–9611.

[15] O. Yassine, O. Shekhah, A.H. Assen, H2S sensors: fumarate-based fcu-MOF thin film grown on a capacitive interdigitated electrode, Angew Chem., 55 (2016) 15879-15883.

[16] N.E. Heshka, J.M. Choy, J. Chen, Gas chromatographic sulphur speciation in heavy crude oil using a modified standard D5623 method and microfluidic deans switching, J. Chromatogr. A,1530 (2017) 241-146.

[17] F. Huber, S. Riegert, M. Madel, K. Thonke, H2S sensing in the ppb regime with zinc oxide nanowires, Sensor. Act. B. Chem., 239 (2017) 358-363.

[18] N.S. Lawrence, J. Davis, R.G. Compton, Analytical strategies for the detection of sulfide: A review, Talanta, 52 (2000) 771-784.

19] R.A.K. Nadkarni, ASTM Test Methods for the Analysis of Petroleum Products and Lubricants, World Refin., 6 (2000) 24-30

[20] O.A. Habeeb, R. Kanthasamy, G.A.M. Ali, Hydrogen sulfide emission sources, regulations, and removal techniques: a review, Rev. Chem. Eng., 34 (2017) 9-19.

[21] R. Wedmann, S. Bertlein, I. Macinkovic, et al. Working with “H2S”: Facts and apparent artifacts: nitric oxide, Biol. Chem, 41 (2014) 85-96.