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Determination of trace sulfur in organic compounds by activated Raney nickel desulfurization method with non-dispersive gas detection system

A. A. Miran Beigi,* M. Teymouri, M. Eslami and M. Farazmand

Standard Laboratory, Research Institute of Petroleum Industry, Tehran, Iran.
E-mail: miranbeigiaa@nioc-ripi.org

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A sensitive and precise method for the determination of trace amounts of total sulfur in organic mixtures is described. With this method bonded sulfur is reacted with activated Raney nickel and is reduced to nickel sulfide at 70 °C. Then, the residue is separated on a filter paper and pyrolysed by induction furnace technique for generation of SO_2 which is then detected by a non-dispersive gas detector. This method is ideally suited for the determination of trace amounts of sulfur in petroleum distillates, organic solvents and pharmaceutical species such as antibiotics and vitamins. The effect of olefines and the amount of Raney nickel on the sensitivity and accuracy of the results is investigated. The 3σ detection limit was 100 ng g^{-1} and at 1 μg g^{-1} sulfur in iso-octane, the relative standard deviation ($n = 5$) was ±5.5%.

Introduction

The study of the corroding effect of organosulfur compounds on refining facilities, air pollution control, poisoning of catalysts and effects of their toxicity on living organisms requires the determination of sulfur and its compounds in a variety of matrices at or below 1 μg g^{-1}.[1–6] A variety of routine methods are available for the determination of total sulfur[7–11] and sulfur compounds individually[12–16] which are accepted by different international standards such as ASTM, DIN, ISO, BSI, *etc.* Unfortunately, there are few methods available at ppm or sub-ppm levels which can be applied to different matrices. With some methods, the presence of certain constituents in the sample matrix makes accurate determination impossible. In oxidative pyrolysis techniques, such as combustion flask,[17–21] Bomb,[11,22,23] Lamp[24] and microcoulometric methods,[25–29] chlorine, bromine, heavy metals, aldehydes and nitrogen (such as NO) can interfere. Furthermore, some of the methods are time-consuming and tedious and also have poor limits of detection. The Raney nickel reduction method has been applied for the determination of low concentrations of sulfur in non-olefinic matrices.[30]

In 1959, Granatelli used Raney nickel for the measurement of microgram quantities of sulfur in non-olefinic hydrocarbon solutions.[31] With this method the sample is reacted with activated Raney nickel to convert organically bonded sulfur to nickel sulfide. The addition of hydrochloric acid to the mixture liberates hydrogen sulfide which is absorbed by caustic–acetone solution. Then, the absorbed hydrogen sulfide is titrated with mercuric acetate using dithizone as the indicator. Although a good average recovery (about 95%) was obtained for a variety of types of sulfur compounds, the presence of olefines in the sample, even at 2% concentration, caused considerable error.

High temperature methods[32,33] are used to determine sulfur in liquids and solids, especially in petroleum products, alloys and catalysts. In such methods, the sample is pyrolysed oxidatively and the generated SO_2 is detected using different procedures.[34,35] Nowadays induction furnace gas analyzers use this technique to determine sulfur and carbon in organic and inorganic compounds.[33,36] The determination is rapid but is influenced by the sample matrix and is usually limited to sulfur concentrations greater than 10 μg g^{-1}. In addition, the technique is unusable for low boiling point (less than 170 °C) liquid samples.

In a previous work,[37] we studied the Raney nickel reduction method with voltammetric detection modes, such as differential pulse cathodic stripping (DPCSV) and square wave voltammetry (SWV), for the determination of total sulfur in petroleum distillates and vegetable oils. The 3σ detection limits were 2 ng ml^{-1} and 25 ng ml^{-1} sulfur for DPCSV and SWV, respectively. The linear dynamic ranges covered 2–140 ng ml^{-1} sulfur and 25 ng–10 μg ml^{-1} sulfur for DPCSV and SWV, respectively. The effects of various factors such as scan rate, deposition potential and time, pulse height and concentration of supporting electrolyte were optimized. This paper describes a new method for the determination of total sulfur in organic compounds based on a combination of catalytic reduction and oxidative pyrolysis with non-dispersive SO_2 detection. The method offers several inherent advantages for total sulfur determination. With this method most sulfur forms are quantitatively converted to nickel sulfide.

Since infrared-active gases absorb thermal radiation at wavelengths which are specific to the gas, non-dispersive SO_2 detection is selective. The attenuations resulting from this effect permit measurements of gas concentrations in ranges extending from several μg g^{-1} to 100%.

Preconcentration of sulfur on the surface of activated Raney nickel is the reason for achieving a limit of detection of 100 ng g^{-1} sulfur. The limit of detection of the method can be improved for more demanding applications with increasing amount of the sample to more than 50 g.

Experimental

Reagents and materials

All solvents and reagents were of analytical grade obtained from Merck or Fluka and were used without further treatment. All pharmaceutical samples were obtained from Farabi Pharmaceutic Co. (Tehran, Iran). A stock standard solution of 1000 μg g^{-1} of *tert*-butyl sulfide (TBS) in iso-octane was standardized by the standard method of Raney nickel and used throughout the experiment.[30] The wolfram accelerator and pure iron powder, used for the induction furnace gas analyzer, were obtained from Rosemount Co. (Hanau, Germany).

Apparatus

An induction furnace gas analyzer consisting of a non-dispersive gas detection system, selective to SO_2 (Rosemount Model C-S 5003A) was used in the pyrolysis step after desulfurization of the samples by activated Raney nickel.

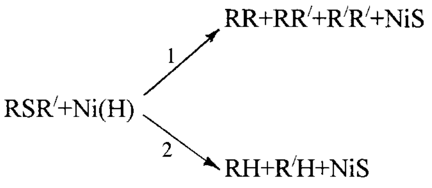
Procedure

For samples containing olefines less than 20, 20–30 and 30–50 wt.% (such as hex-1-ene) weigh at least 0.8, 1.3 and 3.7 g of nickel aluminum alloy, respectively, in a 100 ml polyethylenic beaker and slowly add 10 ml of 2.5 M sodium hydroxide solution. Swirl the beaker gently in a hood until the vigorous evolution of hydrogen has ceased. Allow the reaction to continue overnight in a desiccator without a desiccant. The nickel prepared in this manner is enough to reduce at least 2000 μg sulfur and can also be stored up to one week. Decant the aqueous caustic solution from the beaker containing the activated Raney nickel just before using it. Wash the active nickel thoroughly 3 times with vigorous sprays of water. Allow the nickel to settle each time before the water is decanted. Then rinse the water from the Raney nickel with 15 ml of propan-2-ol and discard the rinsings. Transfer the prepared catalyst to the reaction flask (a 100 ml Erlenmeyer flask) with 10 ml of propan-2-ol and add the required amount of sample so that it contains 10–300 μg of sulfur. Connect a reflux condenser to the flask, in order to prevent evolution of volatile matter from the reaction cell. Then place it in a water bath at 70 °C, allowing the sulfur reduction to proceed for 30 min, while agitating the contents of the flask several times during this period. After the desulfurization has been completed, filter the catalyst with filter paper (Wattman no. 40) and wash 3 times with 10 ml of propan-2-ol (since dried filter paper containing catalyst is flammable, wet the paper with propan-2-ol). Place the wetted filter paper containing the catalyst in the instrument's special crucible and heat to 150 °C with a burner for 5 min and then increase the temperature up to 350 °C for ashing the filter paper (avoid introducing the wetted filter paper into the analyzer because of explosion hazard). Calibrate the sulfur analyzer with 0.147 and 0.0085 wt.% sulfur standard in two different channels and determine the sulfur content of the prepared sample in a suitable channel. For non-olefinic samples, weigh 0.6 g of the alloy and follow the above procedure to prepare the catalyst. Also, select the size of the sample as mentioned above and again follow the procedure.

Results and discussion

Desulfurization process and catalyst activity

Treatment of nickel–aluminum alloy with sodium hydroxide solution is one of the typical techniques for preparing activated Raney nickel.[38] In this reaction aluminum is oxidized to aluminate and hydrogen is evolved vigorously. This catalyst can adsorb a great amount of hydrogen through Van der Waals forces. Two reaction paths are known for the desulfurization process:



(1)

At high temperature and when the catalyst is stored for long periods of time, the reaction proceeds through path 1. Apparently the adsorbed hydrogen decreases at temperatures higher than 100 °C. At low temperature and with freshly prepared catalyst, path 2 is preferred. In the previous work, the average recovery in the determination of 11 standard sulfur samples was 98% ($n = 5$).[37] Further studies in the present work showed that for samples containing thiols and sulfides with linear chains, the recovery was greater than for oxidized sulfur compounds.

We found that the addition of small amounts of platinic chloride to the Raney nickel catalyst, just prior to the start of reduction, enhances the activity of the catalyst. In order to study the promoting effect of platinic chloride, 0.34 g of platinic chloride was added to a suspension of 2.5 g of Raney nickel catalyst in 100 ml of water and the mixture was allowed to stand with occasional shaking for forty-five minutes. During the first few minutes the mixture became opaque, but on standing the colloidal material was settled and a clear green supernatant solution resulted. The clear solution was decanted, the remaining catalyst was washed several times and the combined solutions were diluted to 200 ml volume. The nickel was determined gravimetrically as nickel dimethyl glyoxime. The results found were 0.22–0.24 g while the calculated amount based on the following reaction was 0.2 g. The solution was strongly acidic and contained no platinum.

$$3Ni + PtCl_6^{2-} + 2H^+ \rightarrow Pt + 3Ni^{2+} + H_2 + 6Cl^- \qquad (2)$$

In the case of oxidized sulfur species such as dimethyl sulfoxide and *p*-toluene sulfonic acid, platinized Raney nickel increases the recovery of sulfur to 98.5% in comparison to ordinary Raney nickel (80%). However, the mass of the treated catalyst didn't have an appreciable promoting effect for non-oxidized sulfur compounds.

Development of Raney nickel desulfurization method

Presently the high temperature technique[31] is widely used in the chemical and petroleum industry for the determination of total sulfur at concentrations of more than 50 μg g^{-1}. Induction furnace gas analyzers can determine sulfur in organic and inorganic solid and liquid samples having a boiling point greater than 180 °C.

Unfortunately, interferences such as chlorine, bromine, water content, low limit of detection (LOD) and sample size from 0.05 to 2.00 g limit the application of the sulfur analyzers. For the method developed, we prepared different standards of *tert*-butyl sulfide (TBS) solution in iso-octane in the concentration range of 0.5 μg g^{-1} to 10% by weight. After the preconcentration of sulfur as nickel sulfide on the small surface of the activated Raney nickel, sulfur was determined by an induction furnace analyzer with an IR detection system. Table 1 shows the comparison of calculated and observed concentrations of sulfur. The linear dynamic range was extended from 0.5 μg g^{-1} to several weight percent. With this method, a limit of detection of

Table 1 Obtained results from the determination of sulfur in different standards

No.	Calculated concentration[a]	Average observed concentration[b]	Unit	RSD (%)	No. of determinations
1	0.5	0.50 ± 0.05	μg g^{-1}	10.0	4
2	1	1.00 ± 0.05	μg g^{-1}	6.0	6
3	14	14.1 ± 0.7	μg g^{-1}	5.0	5
4	20	19.6 ± 1.0	μg g^{-1}	5.1	5
5	50	51.4 ± 1.8	μg g^{-1}	3.5	6
6	75	75.8 ± 2.7	μg g^{-1}	3.6	5
7	250	251.3 ± 2.7	μg g^{-1}	1.1	5
8	0.1	0.103 ± 0.001	wt.%	1.0	5
9	1	0.962 ± 0.007	wt.%	0.7	5
10	10	11.232 ± 0.073	wt.%	0.6	4

[a] *tert*-Butyl sulfide. [b] Mean ± *s*.

100 ng g^{-1} was obtained at 3σ, where σ is the estimated standard deviation for triplicate blank determinations. Further improvement in the LOD should be possible by using high purity solvents with a multiple or large sample size up to 150 g. With this method, sample matrix interferences such as those mentioned above, were removed by using Raney nickel and the LOD was improved as compared to the ordinary high temperature methods.

Study of olefine effect

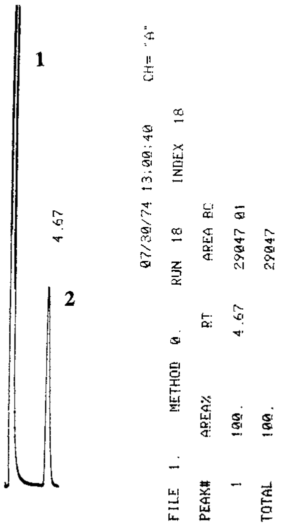
In 1959, L. Granatelli[31] noted that the presence of olefinic compounds in the sample, even at 2 wt.% concentration, causes about 15% error in the results. He never explained the source of the error and olefine interference mechanism. At first, we supposed that the interference is likely a result of an addition reaction between hydrogen sulfide and an olefine (reaction 3) under the experimental conditions, such as a reaction temperature of 70 °C and acidified media, in his work. Therefore, it was required to remove the hydrogen sulfide generation step in a typical Raney nickel method. Furthermore, the complexometric titration by mercuric acetate in the detection of H_2S, as briefly prescribed in the introduction, has become impossible to apply.

$$H_2S + R\text{-}CH{=}CH_2 \rightarrow RCH(SH)\text{-}CH_3 \qquad (3)$$

In order to study the interference mechanism, we replaced the titrimetric method with non-dispersive gas detection. The developed method was based on three major processes of desulfurization, oxidative pyrolysis and SO_2 selective detection. As shown in Fig. 1, we studied the effect of the olefine content on the recovery of sulfur by using three different concentrations of TBS standard solutions (25, 50 and 100 μg g^{-1}) where the weight of nickel–aluminum alloy was 0.6 g and each point was obtained from the average of triplicate measurements. For the points with good recovery in Fig. 1, RSD was ±2.5% while this amount reached almost ±10% for the points with incomplete recovery. It was found that any interference wasn't up to 10 wt.% of hex-1-ene in the determination of sulfur. In concentrations of olefine higher than 10 wt.% the recovery gradually decreased in a pseudologarithmic form and approached 15% (or less) when the concentration of hex-1-ene became 50 wt.% or more. Apparently, the interaction of double bonds with active sites of the catalyst was responsible for the interference in high concentrations of the olefine in the desulfurization step. Thus it can be concluded that the interference occurs in two different steps (desulfurization process and hydrogen sulfide generation) and in each step, it depends on the concentration of olefine in the sample in a typical Raney nickel reduction method.

Chromatographic studies on the filtrate solutions, after the desulfurization process, confirmed incomplete recovery of sulfur in the presence of concentrations of olefine more than 10 wt.%. Fig. 2 shows a chromatogram of the filtrate after desulfurization of a calculated concentration of 100 μg g^{-1} sulfur in TBS standard solution containing 50 wt.% hex-1-ene by using 0.6 g of nickel–aluminum alloy as catalyst. Peak 1 is related to coeluted propan-2-ol and iso-octane (2,2,4-trimethyl pentane) as a solvent while peak 2 shows an observed concentration of 14 μg g^{-1} sulfur in TBS which has remained in solution without conversion to other organosulfur species. When aromatic compounds such as benzene, xylene, toluene, *etc.* were present, a good efficiency of Raney nickel toward the reduction of organosulfur compounds was observed, which allows them to be used as solvents in sample preparation.

Attempts for removing the olefine interference in concentrations of more than 10% by using chemical reagents were unsuccessful. For example, removing the effect of by-products and chemicals remaining from the bromination reaction of double bonds in addition reactions of olefines or their oxymercuration in the reduction of olefinic compounds to alcohol destroyed the activated Raney nickel. As shown in Fig. 3, in order to remove the interference in high concentrations of olefine, we studied the effect of quantities of the catalyst on the recovery of sulfur. Here, test compounds were *tert*-butyl sulfide standard solutions with concentrations similar to those in Fig. 1. Also, the olefine content available in these solutions was fixed at fifty percent by weight. As observed, it was possible to achieve an average recovery of about 98% (using triplicate measurements for each point) by increasing the weight of the catalyst. On the other hand, for high concentrations of sulfur, it



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TOTAL   100.            29047
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Fig. 2 Typical chromatogram of the filtrate after desulfurization process: 1 mixture of propan-2-ol and iso-octane solvents; 2 14 μg g^{-1} sulfur in TBS available in the filtrate solution.

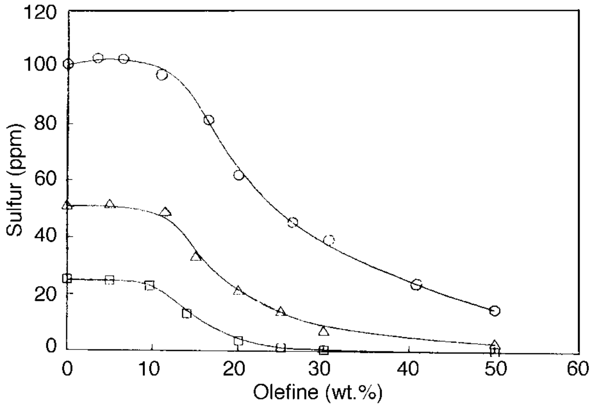

Fig. 1 Olefine interference effect on the recovery of sulfur: weight of catalyst, 0.6 g; no. of determinations, n = 3; test compound, *tert*-butyl sulfide ○ 100 μg g^{-1}, △ 50 μg g^{-1}, □ 25 μg g^{-1}.

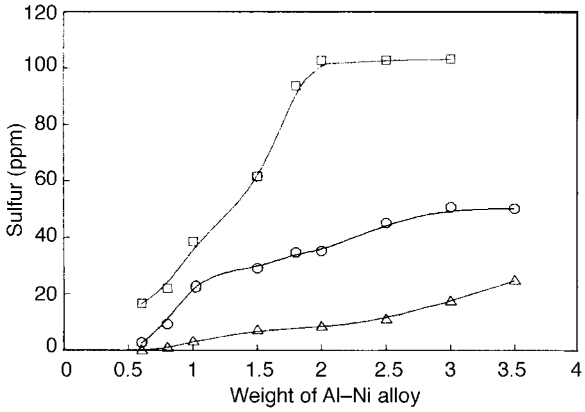

Fig. 3 Effect of catalyst weight on the recovery of sulfur: concentration of olefine, 50 wt.%; no. of determinations, n = 4; test compound, *tert*-butyl sulfide □ 100 μg g^{-1}, ○ 50 μg g^{-1}, △ 25 μg g^{-1}.

Table 2 Determination of sulfur antibiotics available in drugs

Sample	Molecular formula	Molecular weight/g mol^{-1}	Calculated antibiotic content (wt.%)	Observed antibiotic content^a (wt.%)	RSD^b (%)
Vitamin B$_1$ (300 mg)	$C_{12}H_{17}ON_4S.HCl$	337.29	58.82	57.65 ± 1.05	1.82
Penicillin G.L.A (1 200 000 u)	$C_{16}H_{17}N_2NaO_4S$	356.36	59.66	61.96 ± 0.56	0.90
Ampicillin (500 mg)	$C_{16}H_{18}N_3NaO_4S$	371.40	84.75	82.32 ± 1.27	1.54
Amoxicillin (500 mg)	$C_{16}H_{17}N_3O_4S.H_2O$	365.40	84.75	83.58 ± 1.94	1.32
Cephalexin (500 mg)	$C_{16}H_{17}N_3O_4S.H_2O$	365.40	87.72	89.23 ± 2.28	2.56

[a] Mean ± std. dev. [b] $n = 4$.

Table 3 Sulfur determination in many petroleum distillates

	% Sulfur^a		
Sample	Developed method	LECO sulfur analyzer	XRF analyzer
Bahregan (b.p. 175–200 °C)	0.165 ± 0.013	0.17 ± 0.01	0.206 ± 0.001
Maroon (b.p. 200–250 °C)	0.324 ± 0.024	0.33 ± 0.02	0.365 ± 0.001
Foroozan (b.p. 275–300 °C)	1.020 ± 0.050	1.05 ± 0.03	1.004 ± 0.002
Foroozan (b.p. 335-425 °C)	2.116 ± 0.120	2.51 ± 0.04	2.205 ± 0.002

[a] Mean ± *s*

was necessary to use less weight of the catalyst in order to obtain reliable measurements. That is to say that whenever the ratio of organosulfur to olefine is increased, it is necessary to reduce the weight of the catalyst for accurate and precise determination of sulfur. Therefore, it can be concluded that olefines are competing with organosulfur compounds to occupy the active sites of the catalyst.

Sample preparation

Petroleum distillates were used without any treatment and their amounts were selected as prescribed in the experimental section. All pharmaceutical samples available in Table 2, were in the form of tablets, capsules or vials. In order to dilute and dissolve these samples, we used 0.05 M potassium hydroxide solution in water–methanol (1 + 3). The solutions prepared in this manner, can be stored for a long time.

Sulfur determination of samples

In this study, sulfur was determined in a number of petroleum distillates and compared with some standard methods, as shown in Table 3. The analytical results were obtained from the average of the triplicate measurements with a confidence limit of 3σ. Also, the determination of sulfur antibiotics was possible through measurement of the total sulfur in pharmaceutical samples. Table 2 shows the determination of sulfur in these samples and a good agreement between calculated and observed results. The colour of the sample solutions changes gradually from yellow to orange due to incidence of sunlight but this effect can not interfere with the accuracy and precision of the results.

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