

Detection of Combustible Gases by Semiconductor Sensors —Rapid Separation of Hydrogen Sulphide with β, β' -oxydipropionitrile*

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Introduction

Hydrogen sulfide with various concentrations often coexists with combustible gases such as petrochemical tail gas, coal gas, oil-well gas. Chemical sensors provide an alternative to analyse these combustible gases and have such advantages as small sizes, low costs *etc.* However, the catalyst-filled semiconductor gas sensor is susceptible to poison when it is used to detect the combustible gas. With hydrogen sulfide being gradually adsorbed on the noble metal active sites of the sensor, the redox reaction between hydrogen sulfide and the noble metal takes place and the catalyst is poisoned. In this way the selectivity of the gas sensor is deteriorated, and its sensitivity and stability are damaged^[1]. As a special case, petrochemical industrial exhaust gas may contain hydrogen sulfide as high as 97% while the combined concentrations of low carbon hydrocarbons (methane, ethane, propane and propene) is in the range of 0.1%—5%. The quality of the tail gas could be guaranteed if the on-line determination of hydrocarbons concentration is possibly made without hydrogen sulfide disturbance.

Semiconductor gas sensor arrays could be employed to detect hydrocarbons. The feasibility of this detection depends on the possibility of separating the high concentration of hydrogen sulfide in several minutes in advance. The present work is focused on the rapid, complete separation of hydrogen sulfide and hydrocarbons with GC-alike method. The life time of separation apparatus should meet the requirement of on-line detection in industry field.

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Experimental

1 Apparatus and Reagents

A 102G gas chromatograph was used (made by Shanghai Analytical Instrument Plant). A homemade gas sensor array system was setup as a detector after separation. The related work has been published elsewhere^[2]. Methane, ethane, propane and propene were provided by Southwest Chemical Technology Research Institute (Under Ministry of Chemical Industry) in cylinder with a purity of 99.9%. Hydrogen sulfide was produced in the laboratory. The raw reagents, sodium sulfide and sulfuric acid were of analytical-reagent grade. Medical disposable injector and gas balloons were also used.

2 Operation Procedure

A chromatographic column could be used as a separation apparatus since the sample amount needed for the semiconductor sensor detection of gas is small^[3]. However, after the complete computer search of the chemical abstract data base was done, we found that no one had attempted to separate combustible gases from hydrogen sulphide. Comparing the physical and chemical properties of low hydrocarbons with those of hydrogen sulfide, and considering requirements of industry on-line detection, hydrogen sulfide and hydrocarbons could be separated by their polarity difference. After having attempted several separation methods, it was discovered that column adsorption materials could be an effective one. To select the column adsorption material, the commercial stationary phase in gas chromatography could be referred to in this work.

Different from GC, the elution sequence of gas in column has to be considered in the present work. For example, if hydrogen sulfide was eluted between propane and propene, the separation goal of present study could not be attained. The column preparation technology could be borrowed from preparative chromatography. Owing to the easy elution of low alkane, the eluting profile should be hydrocarbons first, then hydrogen sulfide. The other advantage of this sequence is that the tailing of hydrogen sulfide on the column adsorption material doesn't hinder the next detection obviously. The injected gas sample volume is 2ml with a some ratio of 1 to 1 for hydrogen sulfide and hydrocarbons (the ratio among ethane, propane and propene is about 1 : 1 : 1).

Results and Discussion

Three kinds of adsorption materials, *i. e.*, polymer bead, carbon molecular sieve and stationary liquid have been compared in the present work. The columns employed are summarized in Table 1. In this study, the detector used was always a thermal conductivity detector.

Table 1 Adsorption materials used in this work

Column name	Polarity	Type	Provider
404	middle	polymer bead	Shanghai No. 1 Reagents Factory
GDX502	strong	polymer bead	Tianjing No. 2 Reagents Factory
408	stronger	polymer bead	Shanghai No. 1 Reagents Factory
Porapak-T	strongest	polymer bead	Waters Associate Inc. (USA)
TDX601	no	carbon molecular sieve	Shanghai No. 1 Reagents Factory
TDX02	no	carbon molecular sieve	Tianjing No. 2 Reagents Factory
β, β' -oxy -dipropio-nitrile	strongest	stationary liquid	Shanghai No. 1 Reagents Factory

1 The Polymer Bead as an Adsorption Material

The elution time of hydrogen sulfide was compared with that of propene, propene has the longest elution time among the other hydrocarbons, which attributes to its double bond structure, large polarizability and strong inductive force. The experiment results confirmed this inference.

As an adsorption material, the polymer bead possesses such advantages as small tailing, no stationary liquid lose, good repeatability, quick recovery from sample overloading. In this work, the strong polarity of the polymer bead as the adsorption material was first tried. Under the conditions of the column with two meters long, at 84 °C and nitrogen as carrier gas with a 62 mL/min flow rate, the results showed that the elution time of H₂S was 1' 15" while that of propene was 1' 43" on the GDX502 column. Obviously the separation is impossible. The elution time of hydrogen sulfide changed to 50" compared with propene 45" when the 404 column was used. It seems that the separation is possible. However, lowering column temperature to 45 °C caused the elution time of H₂S to extend to 4' 40". There are two main reasons for lowering column temperature. One is to enhance the selectivity of the column, and the other is to reduce gradual degradation of the polymer bead at a high temperature which would reduce the column lifetime. Hydrogen as carrier gas could shorten the elution time to a certain extent, but it would later hinder the semiconductor gas sensor detection. Another 408 column was tried which is similar to the imported PORAPAK R stationary phase. The elution time of H₂S was 48" compared to 57" of propene under the conditions of at 74 °C (column temperature), N₂ as carrier gas and at a 98 mL/min flow rate. Literatures [4,5] indicated that even if the most polar Porapak T was adopted as the column adsorption material, separation between hydrogen sulfide and hydrocarbons was impossible.

2 Carbon Molecular Sieve as Adsorption Material

Having comprehensively considered the two factors of dipole moment and polarizability, the separation effects of TDX601 and TDX02 were examined. The experiment indicated that H₂S came out first, while methane was lagged behind when the column length was 30 cm, the column diameter 2 mm, column temper-

ature 20°C and N₂ was used as carrier gas with a flow rate 50 mL/min. On the TDX02 column, the elution time of H₂S was in the range of 18" to 42", while that of ethane was in the range of 30"—1'; but on the TDX601 column, the elution time of each gas was considerably increased (*e. g.* ethane 5' — 7', propene 4' — 30'). This longer elution time might be attributed to the strong adsorption between hydrocarbon gases and the carbon molecular sieve and non-homogeneous adsorption. Because on-line detection requires several minutes once for every gas, the above elution time of gas is too long for carbon molecular sieve to be used as the adsorption material. Hence the carbon molecular sieve is not suitable in this task.

3 Stationary Liquid as Column Adsorption Material

Stationary liquid could be used as the column adsorption material to separate H₂S and the hydrocarbons. After having tried several liquids, we found that β, β'-oxydipropionitrile can separate H₂S and the hydrocarbons quite well. The results are shown in Table 2.

Table 2 The elution time of H₂S and the hydrocarbons on the column adsorption material

Gas	Hydrogen sulphide	Propene	Propane	Ethane
Elution time	57"—2' 4"	? —55"	? —54"	? —50"

Condition: stationary liquid/support=20/80, column temperature 35°C, column length 3 m, carrier gas flow rate 25 mL/min(H₂).

The time for complete elution of the individual gas was 55 s for propene; 54 s for propane; 50 s for ethane. The time for hydrogen sulphide elution began at 57 s and ended at 2' 4". Therefore the separation between them is feasible. The actual separation of the mixed gases on the column is shown in Fig. 1. A split peak of hydrogen sulfide was observed, which might be due to impurity when hydrogen sulfide was produced because the split peak still existed even if only hydrogen sulfide was injected into the column.

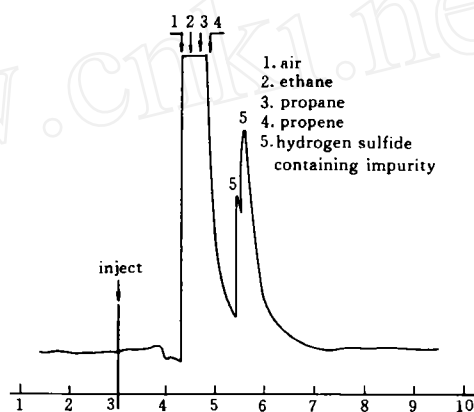


Fig. 1 Initial separation profile of hydrocarbon containing hydrogen sulphide.

Silanized solid support has to be adopted to alleviate peak tailing. The column diameter should be reduced in order to prevent tailing from worsening when N₂ was used as carrier gas. In the meantime, the column length should be increased to improve the separating efficiency of the column. The results are shown in Table 3.

Table 3 The eluting time of H₂S and hydrocarbons on the column adsorption material

Gas	Hydrogen sulphide	Propene	Propane	Ethane
Elution time	1' 14" — 2' 30"	? — 58"	? — 52"	? — 46"

Condition: stationary liquid/support = 20/80, column temperature 30°C, column length 7.45 m, carrier gas flow rate 20 mL/min(N₂)

A little tailing of H₂S was still observed, which, however, does not hamper the system measurement due to the time occupied by the sensors cleaning. In such a way, even if H₂S concentration was as high as 95%, the separation could still be finished. Because the separation was carried out at room temperature, the ordinary phenomenon of stationary liquid lose is not a problem here. Therefore the column life period meets the on-line detection requirements. The low column temperature was chosen in order to increase the static electricity interaction between H₂S and the column adsorption material because they are both polar molecules. Moreover, the detection system was simplified without heating. On the other hand, because the column is similar to the preparation column, the lifetime would be extended greatly by properly increasing the amount of stationary liquid without deteriorating the separation efficiency.

The separation result of the mixed gases on the column is presented in Fig. 2. It is not essential to separate each component of the hydrocarbons because the sensor arrays detect the gases as a whole.

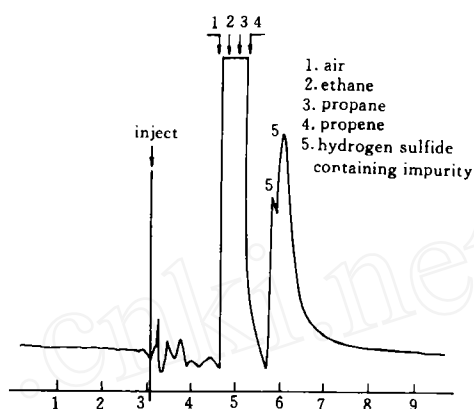


Fig. 2 Separation profile of hydrocarbon containing hydrogen sulphide.

Conclusion

The separation between H₂S and low hydrocarbons has been accomplished by utilizing reversible physical adsorption of stationary liquid, which possesses the advantages of rapid separation and long column life duration. If solenoid switching technology is introduced, nearly the complete separation between 95% H₂S and hydrocarbons can be possible. The successful separation of combustible gases containing a high concentration of H₂S at room temperature makes it feasible the detection of H₂S-containing combustible gas by commercial available semiconductor gas sensor.

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