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of Sulphur Components in Natural Gas

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SELECTIVE SAMPLE ENRICHMENT OF GASEOUS SAMPLES USING A COOLED INJECTION SYSTEM: TRACE DETERMINATION OF SULPHUR COMPONENTS IN NATURAL GAS

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Analytical methods for trace analysis in complex and interfering matrices generally consist of three steps. In a first step the sample is pretreated with the aim to selectively enrich the components of interest. In the second step an efficient separation is performed and finally the target components are detected using a sensitive, and preferably selective, detector. Only if each of these three steps is carefully optimized it is possible to meet the required detection limits with an acceptable level of reliability. In general the three steps identified above are closely interrelated, *i.e.* the demands posed on each of the three steps is determined by the performance of the other two. If, for example, a universal detector is employed, the requirements imposed on the sample pretreatment and separation are much more stringent than in the case of the use of a truly specific detector.

The quantitative analysis of sulphur components in natural gas is a typical example of trace analysis in a complex (and very often interfering) matrix. In Fig. 1 the composition of a typical Dutch natural gas is shown. It is evident from the data in this figure that the analytical problem at hand is extremely difficult. The sulphur species are present in a very complex matrix where hydrocarbons occur at concentrations exceeding those of the sulphur components many times.

A typical dutch natural gas		Sulphur species + required det. limits	
CH_4	600 (g/m³)		
C_2H_6	60	H_2S	0.1 mg/m³
C_3H_8	20	COS	0.1
C_4	8	MeSH	0.01
C_5	4	EtSH	,,
C_6	1.5	DMS	,,
C_7	0.6	etc.	,,
He	0.1	THT	?
N_2	48		
CO_2	28		
Higher hydrocarbons up to C_{24} and higher !			

Figure 1

Natural gas nowadays is a well established contributor to the world energy needs. Moreover, it is an important starting material in a number of large-scale production processes in the chemical industry. The presence of sulphur components in the gas constitutes a serious source of concern because of the corrosive properties of these components as well as their potential hazards for human health and for the natural environment. In addition to this, if natural gas is being used as a reagent in chemical processes, sulphur species present in the gas may adversely affect the performance and life-time of catalysts involved in the reaction.

The required detection limits for sulphur analysis in natural gas are 0.1 mg/m^3 (expressed as mg S/m^3) for H$_2$S and COS and 0.01 mg/m^3 for the mercaptans, sulfides and odorants such as tetrahydrothiophene which are added to the natural gas to impart a characteristic smell to the gas. In this contribution a system will be described that enables the measurement of sulphur components in natural gas at these extremely low levels. The system is based on the selective enrichment of the components of interest on a selective adsorbent, followed by separation on a capillary column and detection of these components using a sulphur selective detector. Selective enrichment of the sulphur species from a large volume of natural gas is carried out by the adsorption/thermal desorption approach. For this purpose the liner of a cooled injection system (KAS or CIS) is packed with a sulphur selective adsorption material. The influence of the nature of the packing material and the operational conditions such as initial liner temperature, flow rate and desorption time were investigated. Because the selection of the detection device to a large extent determines the requirements that have to be imposed on the sample pretreatment, a brief overview of the characteristics of different universal and sulphur selective detectors is presented in a separate paragraph.

Detectors for sulphur analysis

In the development of gas chromatographic systems for sulphur determination the choice of the detector plays a key role as this determines the demands that have to be posed on sample pretreatment and chromatographic separation. Selective detection enables target compounds to be measured while other coeluting compounds are not sensed. If a selective detector is employed it is sufficient if the sulphur components are separated from each other. A complete separation of the sulphur species from the hydrocarbons is not required. In this respect universal detectors such as the thermal conductivity detector (TCD) or the flame ionization detector (FID) behave clearly different. If these detectors are being used, high demands have to be posed on the separation. All non-sulphur containing components have to be separated from the sulphur species as otherwise incorrect peak areas would be obtained. Alternatively, it is possible to remove the interfering hydrocarbons in a selective pretreatment step. Ideally, only the sulphur components from a large volume of gas are introduced into the GC column while the hydrocarbons are eliminated prior to transfer of the sample to the GC column.

Gas chromatography with flame photometric detection (FPD) is nowadays widely used for sulphur speciation in both natural gas as well as petroleum products [1-3]. Although the FPD has proven to be reliable and sensitive it also suffers from a number of important disadvantages such as the well known quenching effect and the inconvenient square dependence of the output signal on the concentrations of the sulphur species [4-8]. More recently the Sulphur Chemiluminescence detector (SCD) was introduced [9]. In this

detector SO, formed during combustion of sulphur containing species in a hydrogen rich FID flame, reacts with ozone to form the electronically excited SO_2^*. The SO is drawn into the SCD by means of a ceramic sampling probe attached to the FID flame housing and a vacuum system. The SO_2^* species relax afterwards by emission of light in the wavelength range of 280-420 nm. The intensity of the light is then measured using a photomultiplier. Important operational SCD parameters that have to be optimized are the position of the ceramic tip in the FID flame and the hydrogen and air flow of the FID.

The ideal detector for sulphur determination in natural gas would be a detector that has a sensitivity sufficiently high to yield the required detection limit at a sample size of some 0.1 to 1 mL. This volume of sample can be introduced easily into a capillary GC column without the need to employ refocussing techniques. Apart from being sufficiently sensitive the detector should also have an infinite sulphur-*over*-carbon selectivity. In this way one can be sure that a high concentration of a hydrocarbon is not accidentally identified as a sulphur containing component. In addition to this, the ideal detector is free of quenching which means that the peak area of a sulphur compound is not affected by coelution with other non-sulphur containing species. Finally, the ideal detector would have a wide linear range, would be easy to use, stable, inexpensive *etc*. To investigate how close the various (sulphur selective) detectors are to being the ideal detector, the performance of some six detectors was studied in detail [10]. From the reasoning pointed out above it is clear that especially the sensitivity, the selectivity and the amenability to quenching are important parameters when investigating the possibilities and limitations of the various potential detectors for sulphur analysis. In Table 1 some relevant characteristics of a number of universal and sulphur selective detector are listed. From the results it is clear that for the present purpose, *i.e.* the detection of sulphur components in natural gas, the SCD is the best choice. This detector offers the highest selectivity and sensitivity and has a large dynamic range. Moreover, its response is largely compound independent and free of quenching over a wide concentration range. These properties to a large extent lower the demands posed on sample pretreatment and chromatographic separation, which would be very stringent in case a TCD or an FID is used as the system detector.

Table 1. Characteristics of several universal and sulphur selective detectors.

Detectors	MDA[a] (gS)	LDR[b]	Selectivity (S/C)	Quenching
SCD	5 pg	$> 10^6$	$> 10^6$	No
FPD	0.1 ng	$< 10^{3c}$	$< 10^5$	Yes
TCD	1 ng	$> 10^3$	Not selective	Not selective
MS^{SIM}	4 pg	$> 10^5$	?[d]	No

[a] MDA = Minimum detectable amount (weight of sulphur).
[b] LDR = Linear dynamic range.
[c] On a log-log scale.
[d] Depends on mass resolution.

Design considerations for the development of systems for sulphur analysis in natural gas

When the detection system that is to be used for detection of the sulphur components has been selected the requirements that have to be met by the sample introduction step and the required quality of the chromatographic separation are known. From the detection limits of the detector and the required minimum detectable concentration in the gas sample the amount of natural gas that has to be introduced can be calculated. Next, the selectivity and the quenching behaviour of the detector determine the required quality of the preseparation and the actual chromatographic separation. Below the design criteria of a system for sulphur analysis in natural gas based on the use of an SCD detector for detection will be discussed in more detail.

Injection volume
As already mentioned before the required detection limits in the natural gas sample are 0.01 mg (S)/m^3. The detection limit of the SCD is 5 pg S, as can be seen from Table 1. This means that the required injection volume is 0.5 mL. For a reliable quantitative analysis in a real sample, however, a safety margin of a factor of 5 to 10 is generally included. This means that the desired injection volume is 5 mL. More precisely, if a selective enrichment step is incorporated in the set-up the sulphur compounds from 5 mL of natural gas have to be retained inside the packed liner of the cooled PTV injector while at the same time the hydrocarbons from this sample are eliminated.

Required quality of (pre)separation
It is evident that for a reliable speciation and quantification of the various sulphur components in natural gas an adequate separation of the individual sulphur peaks is required. As the number of sulphur compounds that are present in natural gas (at a concentration level that can give rise to environmental or catalyst problems) is limited, this separation is not too complex. In general the cluster H$_2$S/COS is the most difficult peak pair. Various columns or column combinations (both packed and capillary) for sulphur separation have been discussed in literature [11]. Some problems sometimes arise from the reactive and adsorptive nature of the sulphur species [12]. This, however, is beyond the scope of the present contribution.

Whether or not it is necessary to separate the individual sulphur species from the hydrocarbons in the gas sample depends on the quenching behaviour of the detector. Because (after a careful optimization!) the SCD is free of quenching it is possible to accurately detect and quantify a sulphur compound even if this compound coelutes with a hydrocarbon. Hence, there is no need to chromatographically separate the sulphur compounds from the hydrocarbons. This, by the way, would be extremely difficult due to the extremely large number of different hydrocarbons present in the gas sample. Apart from the quenching behaviour of the detector, also the selectivity of the detector has to be considered. If the detector has a poor selectivity, non-sulphur containing compounds could incorrectly be identified as being sulphur species. The detector employed in the present study has a S/C selectivity better than 10^6. This means that the detection limits of the detector for hydrocarbons are at least 10^6 times higher than for sulphur species. In the present study we aimed at sulphur detection limits of 0.01 mg/m^3. At a Sulphur-*over*-Carbon selectivity of 10^6 this means that the detection limits for the hydrocarbons are higher than approximately 10^4 mg/m^3. Hydrocarbons that are present at concentrations in

excess of this value will show up as peaks on the SCD chromatogram. To avoid that such peaks are inadvertently identified as sulphur components it is preferable to eliminate these components in the sample preparation step. Hydrocarbons that occur at lower concentration levels do not hamper correct operation as these components are not detected by the selective detector. For the particular case of the average Dutch natural gas this means that methane, ethane and propane have to be eliminated in the sample preparation procedure. Higher hydrocarbons do not have to be eliminated as these components are not sensed by the detector.

Selective enrichment

Adsorption followed by thermal desorption is nowadays widely used to introduce large volumes of gaseous samples onto capillary GC columns. This technique is, strictly spoken, not a large volume sampling technique because not the entire sample is injected. Merely the components of interest from a large volume of gas are transferred onto the column. Adsorption/thermal desorption is hence a selective technique. Only the components of interest are enriched and transferred to the column. The other components are eliminated. The choice of the adsorbent plays an important role in this process. The adsorption material should quantitatively trap all sulphur components from gas volume of at least 5 mL. Methane, ethane and propane should not be retained by the material. Due to their high concentrations these components would give an appreciable signal on the SCD despite the excellent selectivity of this detector. Moreover, the sulphur components should be desorbed quantitatively and rapidly from the adsorbent at mild temperatures. Finally, the material should exhibit a good thermal stability.

In the present study some eight different adsorption materials were investigated on the basis of the properties specified above. In particular the ability of the materials to retain sulphur species while at the same time hydrocarbons can be eliminated was evaluated. An overview of the properties of a number of selected adsorption materials is presented in Table 2.

Properties of investigated adsorption materials

Material	Polarity	Surface Area m/g	Mesh	Desorption temp °C
CP Wax 51 (10%)	Very polar	?	60 - 80	150
Porapack Q	Slightly polar	500 - 700	50 - 80	180
Porapack T	Very polar	250 - 300	80 - 100	170
Chromosorb 102	Slightly polar	300 - 500	80 - 100	180
Chromosorb 103	non - polar	15 - 25	80 - 100	180
Chromosorb 104	Very polar	100 - 200	80 - 100	180
Chromosorb 105	Med. polar	600 - 700	80 - 100	180
Chromosorb 107	Polar	400 - 500	60 - 80	180

Table 2

The properties of the materials with respect to the selective enrichment of sulphur from natural gas was evaluated in a series of model experiments. The equipment used in these experiments is shown schematically in Figure 2. It consisted of a Gerstel KAS II (Gerstel Mülheim a/d Ruhr, Germany), an HP 5890A GC (Avondale, USA), a DKK cryofocusser cold trap (ATAS Veldhoven, the Netherlands) and a Sievers SCD 350 with an Gerstel adjustable probe assembly.

Determination of sulphur components in natural gas
Instrumentation
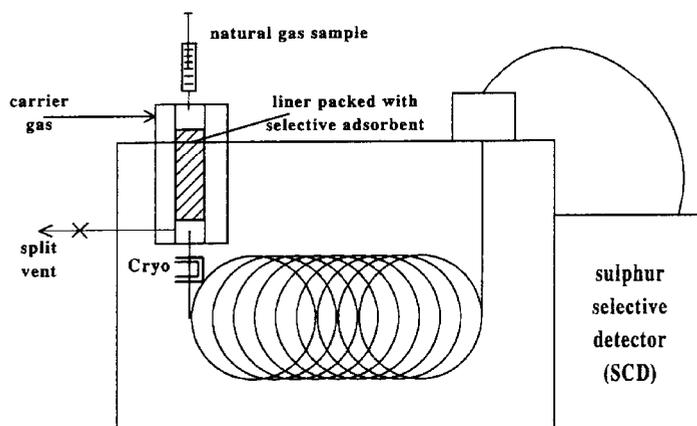
Figure 2

The adsorption material to be investigated was packed into the liner of the PTV injector, held in place at both ends by two small plugs of deactivated glass wool. This packed liner was than conditioned under Helium at a temperature about 20°C above the desorption temperature used in subsequent experiments. Care was taken not to exceed the maximum allowable temperature of the material.

The sulphur mixtures and the normal alkanes were introduced into the PTV liner at sub-ambient initial temperature (-75°C, 60°C and -30°C, respectively). The liner, still held at sub-ambient initial temperature, was than purged with Helium at a flow rate of 100 mL/min. In this step the actual elimination of the hydrocarbons occurs. After purging the liner with helium for some time the split valve was closed and the liner was heated to the desorption temperature. Simultaneously the oven temperature program was started and the chromatogram was recorded. Finally, recoveries of the sulphur species and the alkanes were calculated relative to a cold splitless injection. To obtain sharp peaks a CO_2 cooled cryotrap was employed. Under some conditions CO_2 cooling was found to be insufficient. Therefore, the cryotrap will be replaced by a nitrogen cooled device in the future. Care was taken to avoid contact between the sulphur species and metal surfaces. This to preclude losses due to (ir)reversible adsorption.

During the experimental part of the work the influence of various operational parameters on the recoveries of the sulphur species and the alkanes were studied. Table 2 shows the results obtained for the adsorbent Porapak Q at an adsorption temperature of -75°C, a purge time of 4 min and a purge flow of 100 mL/min. The desorption temperature was 180°C. The desorption time 2 min.

Table 2. Selection of a suitable adsorbent. An example of a poorly selective material.

Component	Recovery [%]
C_1	0
C_2	49
C_3	99
C_4	102
H_2S	100
COS	91
EtSH	88
THT	111

It is clear from the data presented in this table that Porapak Q (under these conditions) is not a suitable adsorbent for the present application. The material shows a lack of selectivity. The sulphur compounds are retained quantitatively but also the alkanes are strongly retained. The material does not meet the requirement that states that methane, ethane and propane should be eliminated completely. With another material better results were obtained[1]. Under optimized conditions this material allows complete elimination of methane, ethane and propane. Butane was retained for only a few percent. The recoveries of all sulphur components were 100%. The selectivity of this new material is illustrated in figure 3. Figure 3A shows a reference chromatogram of an alkane test sample that was used for measuring the recoveries of alkanes. The test mixture contained the alkanes C_2 to C_9 and was injected in the cold splitless mode. Figure 3B shows the chromatogram that is obtained when the test mixture is injected into a cooled liner packed with the adsorbent. After flushing the injector with a helium flow of 100 mL/min for 7 minutes the hydrocarbons up to C_4 were completely eliminated.

Figure 3   A   B

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[1] The name of the material can not be disclosed at this moment due to patent reasons.

In Figure 4 the results of a similar experiment but now with sulphur species are given. Figure 4A shows a cold splitless injection of the test mixture. Figure 4B shows the chromatogram that is obtained after adsorbing the sulphur species on the adsorbent and flushing it again for 7 minutes with a high flow of Helium. From the Figs. 3 and 4 it is clear that the sulphur components are quantitatively retained at conditions under which the lower alkanes are eliminated completely. This adsorption material clearly provides the selectivity required for the enrichment of sulphur components in a natural gas matrix.

Selection of adsorbent
Selective enrichment

Adsorbent = x
Purge time = 7 min
Purge flow = 100 ml/min
PTV: -75 to 180°C at 5°C/s

Sulphur compounds

Cold splitless reference   Adsorption / purge / desorption

Figure 4   A   B

It is interesting to compare the elution times of H_2S and COS in the two chromatograms shown in Fig. 4. Whereas these components are separated when they are injected in the cold splitless mode, coelution occurs when sampling is performed using adsorption and thermal desorption. This is due to the preseparation that occurs in the packed liner. In the case of the cold splitless injection an empty liner was used. Hence, the observed separation is caused by the capillary column solely. If, on the contrary, a packed liner is used for preconcentration, a partial separation occurs already in the liner. The system basically behaves as a multidimensional set-up. A preseparation is performed on the packed liner. This packed liner in principle closely resembles a short packed column. Unfortunately, elution from the liner occurs in reverse order as compared to that on the capillary column. The result is coelution of the H_2S and the COS peak at the end of the chromatographic column. This problem can easily be solved by incorporating a more efficient cold trap in the set-up.

An example of a separation of a true natural gas sample is given in Figure 5. 200 mL of natural gas is pumped through the liner at a temperature of -75°C and a flow rate of 100 mL/min. The upper line (dotted) in the chromatogram shows the FID trace. From this it is clear that the matrix of the natural gas is indeed very complex. The bottom trace (drawn line) shows the SCD chromatogram. Due to the extremely large injection volume even ultra-trace levels of the individual sulphur species can be detected.

Analysis of natural gas

Sample volume: 200 ml

Figure 5
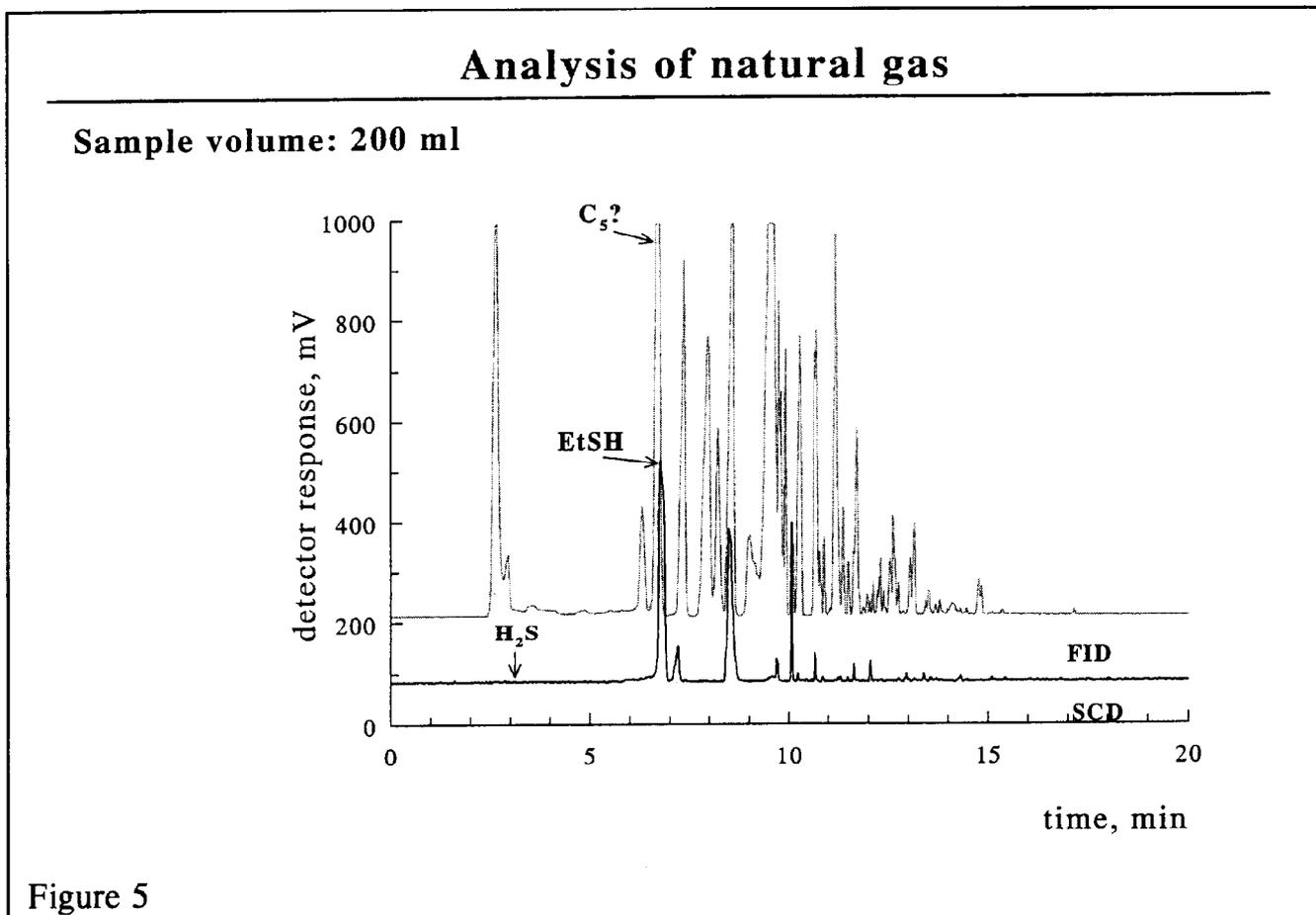
Conclusions

The keyword in the analysis of trace concentrations of sulphur components in natural gas is selectivity. The best system for quantitative analysis of low concentrations of sulphur containing species combines the selectivity and sensitivity of the sulphur chemiluminescence detector with an efficient gas chromatographic separation. A selective enrichment of the sulphur species is of utmost importance. Only if each of these three steps are optimized reliable results can be obtained. Selective enrichment can be performed inside the liner of a cooled PTV type injector. If the liner of the injector is packed with a polar adsorbent sulphur species from large sample volumes can be enriched on the packing material while at the same time hydrocarbons are eliminated. The instrumentation is easy to use and cheap in comparison with dedicated adsorption/thermal desorption instruments. As there is no transfer line between the adsorption unit and the GC the risk of loosing sulphur components by adsorption is minimized. The system is also applicable to other analytical problems related to the determination of low levels of components of interest in a complex gaseous matrix.

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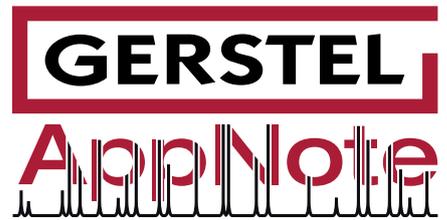
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