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Improved Method for the Determination of Sulfur Components in Natural Gas

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Key Words:
Natural gas analysis
Sulfur components
Adsorption-purge-thermal desorption
Programmed temperature vaporizer
Ultra-thick film apolar capillary column

Summary
Determination of trace concentrations of sulfur components in natural gas is a true analytical challenge. Only analytical procedures based on gas chromatography can meet the sensitivity and accuracy requirements dictated by environmental regulation institutions and modern chemical industry. In the present contribution the sample pretreatment and chromatographic separation steps have been evaluated and optimized based on the use of a flame-based sulfur chemiluminescence detector (SCD) for target compound detection.

The proposed instrument consists of a programmed temperature vaporizing (PTV) injector employing a liner packed with Chromosorb 104, a 4 μm thick film apolar column and a flame-based SCD. Using a 13 mL sample loop the detection limit achievable with the new method is 3 μg S/m³. The precision of replicate measurements is generally in the range of 5-15% relative standard deviation. Lower detection limits can be achieved by preconcentrating larger sample volumes, e.g. 100 mL.

1 Introduction

1.1 Background Information

Natural gas is a well-known source of energy of ever increasing importance [1]. Moreover, natural gas is also used as a starting material in many large-scale chemical processes. The composition of natural gas varies according to its origin. Apart from its main constituent methane, it contains higher hydrocarbons, helium, nitrogen, and carbon dioxide. Moreover, natural gas often also contains sulfur components. Due to their toxicity, corrosive properties, and adverse effects on catalyst performance, a number of analytical procedures exist aiming at the analysis of these components in natural gas samples. The group of components that should be analyzed includes hydrogen sulfide, carbonyl sulfide, the C₁ to C₄ mercaptans, lower sulfides and odorants, such as for example tetrahydrothiophene (THT), added to the gas to impart a characteristic smell for safety purposes.

Standardized methods for the determination of sulfur species in natural gas have been published by the International Organization for Standardization (ISO) [2-7]. These methods can be classified as either conventional techniques (Wickbold, Lingener) or modern instrumental techniques (GC). In the most recent method, ISO standard 6326-4 [6], the sulfur components are separated using a temperature programmed 1.2 m × 2 mm column packed with styrene/divinylbenzene porous polymer beads (80 - 100 mesh) and detected with a sulfur-selective flame photometric detector (FPD). The detection limit is approximately 0.1 mg S/m³.

The ISO method 6326-4 yields the concentrations of the individual sulfur components in the gas. The total sulfur concentration can then be obtained by summing the equivalent S-weights of the individual components. The chromatographic separation procedure incorporated in ISO 6326-4 provides sufficient separation for all sulfur components. Unfortunately, however, it still has a number of problems, most of which originate from the use of flame photometric detection. The selectivity of the flame photometric detector (FPD) is limited and although fairly selective, this detector still responds to high concentrations of non-sulfur components. Moreover, high concentrations of hydrocarbons coeluting with a sulfur containing component can quench the sulfur signal. Finally, the response of the FPD is inherently non-linear and often compound dependent. For these reasons, the concentration of the sulfur species to be determined is limited to the range of 0.1-30 mg S/m³.

For routine natural gas analysis, the detection limits and the reliability of the analytical results achievable by GC with FPD detection are within the desired range. More stringent environmental regulations as well as higher demands currently being posed on the purity of natural gas feed-stocks for chemical processes, however, force analytical chemists to develop new analytical methods that allow the accurate and reliable determination of sulfur in natural gas at concentrations well below the limits currently achievable. For these new methods the detection limits should be around 0.01 mg S/m³. Table 1 gives the composition of a typical Dutch natural gas [8]. The complexity of the natural gas matrix and the extremely low detection limits required make sulfur determination in natural gas a typical example of analyses at trace levels in a complex and interfering matrix. In this situation the analytical methods employed often require the use of selective preconcentration/enrichment techniques. Only if this step and the subsequent separation and detection are carefully optimized, it is possible to meet the required sensitivity limits with an acceptable level of reliability.

When the detection system that is to be used for detection of the sulfur components in the gas sample 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
Improved Determination of Sulfur Components in Natural Gas

Table 1. Composition of a typical Dutch natural gas (Groningen gas) [8].

<table>
<thead>
<tr>
<th>Component</th>
<th>Concn. (mol%)</th>
<th>Concn. (g/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>81.3</td>
<td>580</td>
</tr>
<tr>
<td>Ethane</td>
<td>2.85</td>
<td>38.3</td>
</tr>
<tr>
<td>Propane</td>
<td>0.37</td>
<td>7.3</td>
</tr>
<tr>
<td>Butanes</td>
<td>0.14</td>
<td>3.64</td>
</tr>
<tr>
<td>Pentanes</td>
<td>0.04</td>
<td>1.29</td>
</tr>
<tr>
<td>Hexanes*</td>
<td>0.05</td>
<td>1.93</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>14.35</td>
<td>180</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.89</td>
<td>17.52</td>
</tr>
</tbody>
</table>

The concentration assigned under the term "hexanes" includes also higher hydrocarbons, which are present at very low concentrations.

The minimum detectable concentration in the gas sample the amount of natural gas that has to be introduced onto the column can be calculated. Next, the selectivity and the quenching behavior of the detector determine the required quality of the preseparation and the actual chromatographic separation.

1.2 Sample Pretreatment – Sulfur Selective Enrichment

The sulfur chemiluminescence detector (SCD) has been commercially available for about seven years. Sulfur chemiluminescence detection is based on the reaction of SO formed during combustion of sulfur species with ozone to form electronically excited SO₂. For combustion the original SCD used a hydrogen rich FID flame. An advantage of this approach is that SCD and FID signals are obtained simultaneously. More recently, a flameless SCD was introduced. This instrument uses a catalytic converter to combust sulfur species to SO. The latter instruments has a slightly improved sensitivity and selectivity relative to the flame-based SCD.

In a previous publication [9] we have already pointed out that the SCD is the best choice for sulfur determination in natural gas. The detection limit of the flame-based SCD used in the present work is approximately 15 pg of sulfur if the detector optimized for being quenching-free [9]. This, together with the required detection limit of 0.01 mg S/m³, means that the injection volume must be approximately 1.5 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 in order to meet the desired quantification limits at least some 15 mL of natural gas have to be introduced onto the GC column. More precisely, the sulfur compounds from some 15 mL of natural gas have to be retained in some type of an adsorption device while at the same time the hydrocarbons from this sample are eliminated as completely as possible. This is necessary because of detector selectivity constraints (see below).

The SCD, employed in the present study, has a Sulfur-over-Carbon selectivity better than about 10³. The required sulfur detection limits in the present study were 0.01 mg S/m³. At a selectivity value of 10³ this means that the detection limit for the hydrocarbons is 10 g C/m³. Hydrocarbons that are present at concentra-

tions in excess of this value will show up as peaks on the sulfur selective SCD chromatogram. To avoid the risk that such peaks are incorrectly identified as sulfur components it is desirable to eliminate these components in the sample preparation step. For the particular case of the average Dutch natural gas (Table 1) this means that methane, ethane and preferably also 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 SCD detector.

Adsorption followed by thermal desorption is an interesting approach for selective enrichment of sulfur species from a large volume of natural gas. In our case the adsorption – purge – thermal desorption (APD) technique is carried out outside the liner of a programmed temperature vaporizing (PTV) injector. The liner of the injector is packed with a selective adsorption material and kept at a controlled temperature. During adsorption and purging the split exit of the injector is open. After purging the split exit is closed and the components are desorbed and transferred to the column by heating the injector. An advantage of the use of a PTV injector for adsorption-purge-desorption is the fact that in this set-up there is no transfer line. The components that are desorbed from the adsorption material are transferred directly into the column. This minimizes the possibility for adsorption losses of the sulfur species.

The choice of the adsorbent plays an important role in the APD technique. The adsorption material should quantitatively trap all sulfur components from a gas volume of about 15 mL. Methane and ethane (and preferably also 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 sulfur components should be desorbed quantitatively and rapidly from the adsorbent at mild temperatures. Finally, the material should exhibit a good thermal stability. Adsorption characteristics towards sulfur compounds of a number of adsorption material have been reported. The range of materials studied in literature includes Tenax GC [10-15], Carbopak B, Porapak Q or P, Chromosorb 102, Molecular Sieve 5A and 13X [10], XAD-2, -4,-7 [12]. The poor selectivity and excessive retention power, however, limits the use of these materials for selective enrichment of sulfur components from natural gas.

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 sulfur species while at the same time hydrocarbons can be eliminated was evaluated.

1.3 Chromatographic Separation

As indicated above the flame-based SCD employed in this study is, after careful optimization, quenching free over a wide concentration range [9]. This means that the sulfur components do not have to be separated from the interfering hydrocarbons. They, however, still have to be efficiently separated from each other to avoid errors in quantitation. The column chosen should give sufficient resolution for volatiles as for example COS and H₂S, which is the most critical cluster, while at the same time show no band broadening for high boiling component such as butyl-mercaptan (BuSH) and tetrahydrothiophene (THT). Moreover,
the column should not give rise to adsorption losses, a problem which is very characteristic for sulfur components.

1.4 Application to Natural Gas Samples

The selection of a suitable adsorption material and a capillary column results in the proposal of an instrument, which has been tested using real natural gas samples. The new procedure was evaluated in terms of sensitivity, accuracy and precision. Permeation devices were used to generate gas calibration mixtures. The use of permeation tubes has been preferred over diffusion devices and gas standard cylinders [16] owing to their better accuracy, precision and stability of generated concentrations, minimal risk of adsorption losses and ease of use.

2 Experimental

2.1 Chemicals and Samples

For the investigation of the properties of the different adsorption materials mixtures of sulfur compounds were made-up in glass vials. The first (gaseous) mixture contained H₂S and COS in hydrogen (dilution gas) at concentrations of about 5% (v/v) of the former and 1% (v/v) of the latter. Ethylmercaptan (EtSH), dimethyl sulfide (DMS), and iso-propylmercaptan (i-PrSH) were injected as pure liquids (10 μL each) together with butylmercaptan (n-BuSH) and THT (20 μL pure liquid each) into a 2 L glass vial washed with methanol and acetone before use. Methane, ethane, propane, and butane were used as pure gases. The alkanes pentane up to decane were introduced as a liquid mixture, which was prepared by mixing 10 μL of the pure liquids. For analysis, 10 μL of each gas or gas mixture and 1 μL of the liquid solution was injected. The FID was employed for the analysis of the alkane mixtures, while sulfur compounds were analyzed using the SCD.

Eight adsorbents were studied experimentally. The ideal adsorbent quantitatively retains sulfur components from a large volume of gas while at the same time showing no interaction with the sulfur-free species (hydrocarbons). An overview of the properties of these adsorption materials is presented in Table 2. All materials were purchased from Chrompack (Bergen op Zoom, the Netherlands).

Table 2. Properties of investigated adsorption materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Abbrev.</th>
<th>Type*</th>
<th>Polarity</th>
<th>Surface area (m²/g)</th>
<th>Mesh</th>
<th>Max. desorp. temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP Wax 51 (10%)</td>
<td>CPWax51</td>
<td>EVB-DVB</td>
<td>very polar</td>
<td>500-700</td>
<td>60-80</td>
<td>150</td>
</tr>
<tr>
<td>on Chromosorb AW</td>
<td>PorQ</td>
<td>EGDMA</td>
<td>slightly polar</td>
<td>250-300</td>
<td>50-80</td>
<td>180</td>
</tr>
<tr>
<td>Porapak T</td>
<td>PorT</td>
<td>STY-DVB</td>
<td>very polar</td>
<td>300-500</td>
<td>80-100</td>
<td>170</td>
</tr>
<tr>
<td>Chromosorb 102</td>
<td>Chr102</td>
<td>Polystyrene</td>
<td>non-polar</td>
<td>15-25</td>
<td>80-100</td>
<td>180</td>
</tr>
<tr>
<td>Chromosorb 103</td>
<td>Chr103</td>
<td>ACN-DVB</td>
<td>very polar</td>
<td>100-200</td>
<td>80-100</td>
<td>180</td>
</tr>
<tr>
<td>Chromosorb 105</td>
<td>Chr105</td>
<td>Polyaromatic</td>
<td>moder. polar</td>
<td>600-700</td>
<td>80-100</td>
<td>180</td>
</tr>
<tr>
<td>Chromosorb 107</td>
<td>Chr107</td>
<td>Acrylic ester</td>
<td>polar</td>
<td>400-600</td>
<td>60-80</td>
<td>180</td>
</tr>
</tbody>
</table>

* STY = styrene; DVB = divinyl benzene; ACN = acrylonitrile; EVD = ethylvinylbenzene; EGDMA = ethylene glycol dimethacrylate.
Helium was used as carrier gas with a column head pressure of 10 psi. The total flow rate was set at 100 mL/min unless stated otherwise.

For generating calibration gas mixtures two permeation tubes were used. A COS permeation tube with a loss rate of 450 ng/min (±25% at 30°C) and a MeSH permeation tube with a loss rate of 39 ng/min/cm (±10% at 30°C) (VICI Metronics, Santa Clara, CA, USA) were purchased from Bester (Amstelveen, the Netherlands). These permeation tubes were inserted into the oven of a DKK Model GST-1 calibration gas generator (DKK Corporation). The temperature was set to 30°C. Air was used as the dilution gas at a flow rate of 200 mL/min.

The detection system used was a Sievers SCD 350B purchased from Gerstel Benelux B.V. (Brielle, the Netherlands). The SCD is mounted on top of the FID using an adjustable adapter (Gerstel). The temperature of the FID housing was set at 250 °C. The hydrogen flow was 195 mL/min and air 400 mL/min. Pure oxygen with a flow rate of 50 mL/min was used for the SCD ozone generator.

A two-channel Nelson Omega 5.2 data system (Perkin-Elmer, Norwalk, CT, USA) was used for collecting data from both the FID and SCD simultaneously.

Gaseous and liquid samples used in the experiments for the adsorption material investigation were injected into the PTV injector using gas- or liquid-tight syringes, respectively. The injection volume was 10 µL for the gaseous mixtures and 1 µL for the liquid mixtures of higher alkanes. For column investigation and optimization and real natural gas analysis gas a sampling valve was used to introduce the gas samples into the PTV. This was six-port VICI AG Valco Europe (Schenkon, Switzerland) equipped with a 1 mL, 13 mL, or 100 mL sample loop, respectively. Sample loops were made from PTFE tubing. A schematic diagram of the instrumental set-up is shown in Figure 1.

2.3 Experimental Procedures

2.3.1 Adsorption Material Investigation

The properties of the materials with respect to the selective enrichment of sulfur from natural gas were evaluated in a series of model experiments. The adsorption material to be investigated was packed into a glass liner of the PTV injector, held in place by two small plugs of deactivated glass wool. The total mass of adsorbent used was 15 to 20 mg, resulting in a bed with a length of approximately 4 cm. The packed liner was then 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 sulfur mixtures and the normal alkanes were introduced into the PTV liner at sub-ambient initial temperature (−75°C and −60°C, respectively). The liner, still held at sub-ambient initial temperature, was then 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 sulfur species and the alkanes were calculated from peak areas relative to a cold splitless injection. To obtain sharp peaks a (gaseous) CO₂ cooled cryotrap was employed. Care was taken to avoid contact between the sulfur species and metal surfaces in this way precluding losses due to (ir)reversible adsorption.

2.3.2 Sampling Procedure for Natural Gas Analysis

Upon injection of the gas sample the PTV liner is cooled to the adsorption temperature (−75°C). During this stage of the procedure the switching valve is in position A and the split valve in position B (see Figure 1) to lead the carrier gas through the sampling valve. Next the content of the sample loop is transferred to the PTV liner by switching the sampling valve from "load" to "inject". Depending on the volume of the sample loop, i.e., 1 mL, 13 mL or 100 mL, respectively, the transfer times used were increased from 30 s to 5 min. During sample transfer the sulfur components are trapped inside the liner. The helium flow rate during transfer was 100 mL/min. After completing transfer the liner was flushed with helium for 4 min. at a flow rate of 100 mL/min. Finally the split valve is closed (changed to position A), the temperature programs of both the PTV and the GC oven are started, and the chromatogram is recorded. The calibration process involved analysis of the external standards prepared using the permeation tubes. For calibration the gas sample in Figure 1 was replaced by the gas standard and the procedure described above was repeated.

3 Results and Discussion

3.1 Adsorption Material Investigation

During the experimental part of the work the influence of various operational parameters on the recoveries of the sulfur species and the alkanes were studied. Table 3 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.

Figure 1. Schematic diagram of the final instrument for sulfur determination in natural gas as constructed for use in the laboratory. Sampling valve is in the load position.
Table 3. Selection of a suitable adsorbent.
An example of a poorly selective material.
Recoveries of some alkanes and sulfur compounds on Porapak Q.

<table>
<thead>
<tr>
<th>Component</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0</td>
</tr>
<tr>
<td>Ethane</td>
<td>49</td>
</tr>
<tr>
<td>Propane</td>
<td>99</td>
</tr>
<tr>
<td>Butane</td>
<td>102</td>
</tr>
<tr>
<td>H₂S</td>
<td>100</td>
</tr>
<tr>
<td>COS</td>
<td>91</td>
</tr>
<tr>
<td>EtSH</td>
<td>88</td>
</tr>
<tr>
<td>THT</td>
<td>111</td>
</tr>
</tbody>
</table>

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 sulfur compounds are retained quantitatively, but also the alkanes are strongly retained. The material does not meet the requirement that states that methane and ethane (and preferably also propane) should be eliminated completely.

Tables similar to Table 3 were prepared for each of the adsorption materials investigated under the different experimental conditions studied. Below a summary of the results is given (Table 4). The purge time used in each experiment was 7 min at a purge flow rate of 100 mL/min. The initial PTV temperature was set at −75 °C. At higher initial temperatures as for example −60 °C H₂S and COS showed almost immediate breakthrough on most of the adsorption materials investigated. From Table 4 it is also clear that the polar materials have a better selectivity than the non-polar ones. Only polar materials can provide the required selectivity.

Table 4. Recoveries of the investigated components using the APD technique with 7 min helium purging (100 mL/min) at −75 °C.

<table>
<thead>
<tr>
<th>Component</th>
<th>CP Wax51</th>
<th>PorQ</th>
<th>PorT</th>
<th>Chr102</th>
<th>Chr103</th>
<th>Chr104</th>
<th>Chr105*</th>
<th>Chr107</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ethane</td>
<td>0</td>
<td>15</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Propane</td>
<td>0</td>
<td>96</td>
<td>70</td>
<td>71</td>
<td>19</td>
<td>2</td>
<td>94</td>
<td>90</td>
</tr>
<tr>
<td>Butane</td>
<td>0</td>
<td>99</td>
<td>98</td>
<td>70</td>
<td>56</td>
<td>15</td>
<td>80</td>
<td>88</td>
</tr>
<tr>
<td>Pentane</td>
<td>1</td>
<td>100</td>
<td>91</td>
<td>86</td>
<td>83</td>
<td>75</td>
<td>96</td>
<td>98</td>
</tr>
<tr>
<td>Hexane</td>
<td>1</td>
<td>99</td>
<td>97</td>
<td>89</td>
<td>115</td>
<td>82</td>
<td>100</td>
<td>96</td>
</tr>
<tr>
<td>Heptane</td>
<td>4</td>
<td>97</td>
<td>97</td>
<td>94</td>
<td>103</td>
<td>83</td>
<td>107</td>
<td>98</td>
</tr>
<tr>
<td>Octane</td>
<td>5</td>
<td>93</td>
<td>92</td>
<td>103</td>
<td>107</td>
<td>83</td>
<td>100</td>
<td>97</td>
</tr>
<tr>
<td>Nonane</td>
<td>61</td>
<td>100</td>
<td>84</td>
<td>112</td>
<td>92</td>
<td>84</td>
<td>99</td>
<td>97</td>
</tr>
<tr>
<td>H₂S</td>
<td>0</td>
<td>95</td>
<td>65</td>
<td>91</td>
<td>0</td>
<td>97</td>
<td>105</td>
<td>133</td>
</tr>
<tr>
<td>COS</td>
<td>0</td>
<td>74</td>
<td>109</td>
<td>75</td>
<td>80</td>
<td>105</td>
<td>92</td>
<td>85</td>
</tr>
<tr>
<td>EtSH</td>
<td>0</td>
<td>87</td>
<td>100</td>
<td>90</td>
<td>97</td>
<td>97</td>
<td>104</td>
<td>91</td>
</tr>
<tr>
<td>DMS</td>
<td>0</td>
<td>89</td>
<td>100</td>
<td>102</td>
<td>93</td>
<td>98</td>
<td>98</td>
<td>90</td>
</tr>
<tr>
<td>i-PrSH</td>
<td>0</td>
<td>98</td>
<td>101</td>
<td>96</td>
<td>98</td>
<td>98</td>
<td>99</td>
<td>90</td>
</tr>
<tr>
<td>n-BuSH</td>
<td>2</td>
<td>102</td>
<td>86</td>
<td>83</td>
<td>90</td>
<td>93</td>
<td>91</td>
<td>113</td>
</tr>
<tr>
<td>THT</td>
<td>95</td>
<td>118</td>
<td>75</td>
<td>95</td>
<td>88</td>
<td>106</td>
<td>81</td>
<td>107</td>
</tr>
</tbody>
</table>

* Experiment on Chromosorb 105 was carried out at initial temperature of −60°C.
The best results in terms of sulfur over hydrocarbon selectivity as well as break-through volume were obtained with Chromosorb 104. Under optimized conditions this material allows almost complete elimination of methane, ethane and propane. Butane was retained for only a few percent. The recoveries of all sulfur components were 100%. The break-through volume of the sulfur components of interest on the adsorbent Chromosorb 104 were found to be more than 1 L. The selectivity of this material is illustrated in Figure 2. Figure 2A shows a reference chromatogram of an alkane test sample that was used for measuring the recoveries of alkanes. The test mixtures contained the alkanes C2 to C9 and were injected in the cold splitless mode. Figure 2B shows the chromatogram that is obtained when the test mixtures are injected into a cooled liner packed with the adsorbent. After flushing the injector with a helium flow of 100 mL/min for 7 min the hydrocarbons up to C4 were completely eliminated.

In Figure 3 the results of a similar experiment but now with sulfur species are given. Figure 3A shows a cold splitless injection of the test mixtures. Figure 3B shows the chromatogram that is obtained after adsorbing the sulfur species on the adsorbent and flushing it again for 7 min with a high flow of helium. From Figures 2 and 3 it is clear that the sulfur components are quantitatively retained at conditions under which the lower alkanes are eliminated completely.

It is interesting to compare the elution times of H2S and COS in the two chromatograms shown in Figure 3. Whereas these components are separated when they are injected in the cold splitless mode, coelution occurs when sampling is performed using the APD technique. 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 preseparation occurs in the liner. The system basically behaves as a multidimensional set-up. A preseparation occurs on the packed liner, which in principle closely resembles a short packed column. Unfortunately, elution from the liner occurs in a reverse order as compared to that on the capillary column. The result is poor resolution between the H2S 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 or by using a separation column with a more retentive stationary phase (see also Section 3.2).

The keyword in the analysis of trace concentrations of sulfur components in natural gas is selectivity. From the study described above the adsorbent Chromosorb 104 was found to have the best sulfur compound to hydrocarbon selectivity and loadability among the eight adsorption materials investigated. The break-through volume of the Chromosorb 104 material is well above the lowest achievable initial oven temperature, this column gives the lowest achievable initial oven temperature, this column gives poor resolution between the H2S 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 or by using a separation column with a more retentive stationary phase (see also Section 3.2).

3.2 Column Investigation

Four different columns were evaluated in terms of separation power and analysis time for the separation of the sulfur species of interest.

3.2.1. Non-Polar Thick-Film Column (35 m x 0.32 mm x 1.1 μm CP Sil-5 CB)

The volatility, polarity, desorption, and reactivity of the investigated sulfur components logically lead to the choice of a non-polar thick-film column for their separation. A column with a low phase ratio will give sufficient retention to the volatile compounds investigated in our study.

Figure 4 shows an SCD chromatogram of the sulfur gas mixture on a 1.1 μm thick-film column (phase ratio 75) using cold splitless injection with a 20 μL syringe. For this purpose the PTV was equipped with an empty glass liner and programmed from 30 °C initially, followed by heating to 250 °C at 12 °C/min. The oven temperature was started at 30 °C. It is clear from the figure that at the lowest achievable initial oven temperature, this column gives adequate baseline separation between H2S and COS if syringe injection is used. This, however, is no longer true, when a sample pretreatment procedure based on the APD technique (see Section 3.1) is incorporated in the method. Band broadening is not suf-
Improved Determination of Sulfur Components in Natural Gas

3.2.2 Ultra Thick-Film Non-Polar Capillary Column (30 m x 0.32 mm x 4 μm SPB™-1 SULFUR)

For improving the separation between H₂S and COS an ultra thick-film column (d_f = 4 μm, phase ratio 20) was used. With this column it was expected that a better cold trapping of the components would be obtained. Figure 6 shows a chromatogram of the gaseous sulfur mixture on this column using the APD injection technique. From the figure it can be seen that with this thicker stationary phase the cold trapping effect indeed works more efficiently for the lower boiling compounds, i.e. i-PrSH. Despite this the more volatile components still show some peak broadening and tailing.

3.2.3 CarboPLOT Column (23 m x 0.53 mm x 25 μm CarboPLOT P7, Chrompack)

The Carbo PLOT column provided too much retention for the solutes of interest. Therefore, this column could not be used for the analytical problem at hand.

3.2.4 Pora PLOT Column (30 m x 0.53 mm AT Q)

After the experiments with the CarboPLOT column, a 30 m x 0.53 mm AT Q column (equivalent to a PoraPLOT Q column) was used. A chromatogram of the sulfur compounds separated on this column is shown in Figure 7. As can be seen here an excellent separation between H₂S and COS was obtained, even at a high oven temperature (70 °C). Unfortunately, higher boiling components show some band broadening and their detection limits on this column, therefore, are worse than those obtained on the non-polar column.

From the study described above, it can be concluded that the 4 μm thick-film SPB™-1 SULFUR column and the AT Q column are the best choices for the separation of sulfur components from natural gas. While the former gives good peak shapes for all components of interest and adequate separation of the most critical peak pair H₂S and COS, the latter one provides an excellent...
separation for this cluster even at higher initial oven temperatures. The only disadvantage of this column is the slight peak tailing and band broadening for higher boiling components such as THT. This results in somewhat higher detection limits for these components. It should be emphasized here that the SPB™-1 column gives good results only if it is used in combination with a (CO₂ cooled) cryotrap. The use of a cryotrap is not necessary if an AT Q column is used.

3.3 Application to Natural Gas Analysis

From the evaluatory studies described above it can be concluded that the optimum instrumental set-up for the determination of low concentrations of sulfur containing species in natural gas consists of a selective sample enrichment procedure based on selective adsorption of the components of interest on Chromosorb 104, a separation on a non-polar ultra-thick film column (30 m × 0.32 mm × 4 μm SPB™-1 SULFUR) in combination with a sulfur selective detection device such as the SCD. In this section such an instrument is constructed (Figure 1) and evaluated. The results of the new method are compared with those obtained using the technique currently in use (packed column-FPD).

For the comparative study natural gas samples were analyzed using both the new and the old procedure. Representative chromatograms of the first sample are shown in Figure 8. From this figure it is clear that the new procedure is superior in several aspects. Firstly the new procedure is more selective. No hydrocarbon peaks show up in the chromatogram. Further, the signal-to-noise ratio is better in the new chromatogram leading to improved detection limits. In the new method four peaks (H₂S, COS, MeSH, and DMS) can be seen, of which three can be quantified. In the standardized method only one sulfur peak (COS) can be seen and quantified. Last but not least, the separation efficiency of the new method is higher ensuring the H₂S peak to be fully separated from the COS peak which is the main component. This allows completion of the analysis in a shorter time.

Figure 8. Chromatogram of sulfur components in natural gas sample A analyzed by: A - the new method with a 1 mL sample loop. Chromatographic conditions: see Experimental; B - the standardized method based on packed column GC - FPD. In the order of increasing retention times the peaks are identified as methane, ethane, COS and propane.

<table>
<thead>
<tr>
<th>Compound</th>
<th>std. method</th>
<th>new method 1 mL loop</th>
<th>new method 13 mL loop</th>
</tr>
</thead>
<tbody>
<tr>
<td>conc. (mg S/m³) (%)</td>
<td>conc. (mg S/m³) (%)</td>
<td>conc. (mg S/m³) (%)</td>
<td>conc. (mg S/m³) (%)</td>
</tr>
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<td>0.1001 5.2</td>
<td>0.1001 5.2</td>
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<tr>
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<td>1.4654 4.8</td>
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</tr>
<tr>
<td>EtSH nd</td>
<td>nd</td>
<td>0.0224 8.2</td>
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<tr>
<td>DMS 0.1512</td>
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<td>0.1681 5.5</td>
</tr>
<tr>
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<td>nd</td>
<td>DL</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>nd</td>
<td>0.0136 18.7</td>
<td>0.0136 18.7</td>
</tr>
<tr>
<td>THT nd</td>
<td>nd</td>
<td>0.0069 26.6</td>
<td>0.0069 26.6</td>
</tr>
</tbody>
</table>

a) nd = not detected; b) DL = at the detection limit; c) THT does not occur in untreated natural gas. The peak that elutes at the same retention time as THT may be thiophene, which is often found to be present in petroleum fractions.

Table 5. Comparison of the features of the new analytical procedure and the standardized method.
time and results in more accurate peak area measurements for these two peaks.

If a larger sample loop is used the signal to noise ratio is further improved and also other sulfur components can now be quantified accurately (Figure 9). If a 13 mL loop is used the quantitation limit is 0.01 mg S/m³ (with a signal to noise ratio of approximately 10) and the detection limit is as low as 0.003 mg S/m³ (with a signal to noise ratios of 3). With the set-up which incorporates a 13 mL sample loop it is possible to detect a large number of sulfur components, which are undetectable if the old standardized method is used.

A summary of the results obtained from the analysis of the same sample (natural gas sample A) by the two methods, new- and standardized is shown in Table 5. With the standardized method quantitation was performed using gas standard mixtures taken from calibration gas cylinders. In the new method dynamic generation of calibration standards using permeation devices was employed. This table clearly illustrates the superiority of the new method in terms of detectability. Because of the higher overall selectivity of the method the risk of false positive sulfur identification is also greatly reduced. The precision of peak quantitation, expressed by the RSD of three replicate peak area measurements, is generally in the range of 4 – 9%. Comparing the COS content in natural gas sample A obtained by both methods we can conclude that the accuracy of the new method is within 10% relative to the standardized method. For other components differences were sometimes observed which are most likely due to losses of the sulfur components from the sample because of adsorption/reaction during storage.

Higher boiling sulfur components such as the higher mercaptans and sulfides are present in natural gas at extremely low concentrations. For these components the newly developed method with a 13 mL sampling loop gives peaks at detection limit level (see Figure 9 and 10). A logical approach for the accurate quantitation of these components is to increase the sample volume. For this purpose a direct sampling technique was employed. The natural gas bottle was connected directly to the transfer capillary which was lead into the injector via an open/close valve. When the PTV liner was ready at subambient adsorption temperature, i.e. –75 °C, the carrier gas line was closed and the gas sample line opened. A volumeter was connected to the split vent to control the volume of gas that passed through the PTV liner. After the desired volume of natural gas was pumped through the liner, the sampling valve was closed and the carrier gas line opened to purge the liner. The desorption process and the chromatographic run were started simultaneously 4 min afterwards. Chromatograms of sample B are shown in Figure 11, where the sample volume was 100 mL (A), and 500 mL (B), respectively.

When comparing Figure 11A and Figure 10 it is clear that with larger sample volumes, the detection limits are greatly improved. The sample volume, however, can not be increased unlimitedly. Together with the sulfur components, also the higher hydrocarbons, which are present in natural gas in large numbers and at relatively high concentrations, are adsorbed. These components cannot be eliminated by using longer helium purging times due to their strong interaction with the adsorbent. Large amounts of coeluting hydrocarbons can cause peak broadening of the sulfur species, such as seen from peak No. 4 in Figure 11B. The broadening complicates peak integration and can, hence, lead to quantitation errors. Large hydrocarbon peaks can also show up in the

Figure 10. Chromatogram of sulfur components in natural gas sample B analyzed by the new method with a 13 mL sample loop. Chromatographic conditions: see Experimental. The dotted line is the FID signal (right scale), the full line is the SCD signal (left scale).

Figure 11. Chromatogram of sulfur components in natural gas sample B analyzed by the new method with a sample volume of 100 mL (A) and 500 mL (B), respectively. Chromatographic conditions: see Experimental. The dotted line is the FID signal (right scale), the full line is the SCD signal (left scale).
SCD chromatogram despite the extremely high detector selectivity. For example, the peak between peaks No. 5 and 6 in Figure 11B can incorrectly be identified as a sulfur peak. If flame-based SCD is used for sulfur selective detection it can easily be verified whether a peak in the SCD signal originates from a sulfur containing component or from a high concentration of an alkane. If the peak is an alkane, a very high peak should also appear on the FID trace. If there is no peak or just a small peak on the FID chromatogram, the SCD peak originates from a sulfur component.

Having simultaneous FID and SCD signals is a very large advantage of the flame-based SCD. If other selective detectors are used one can never be sure that a peak is a sulfur peak and not a very high concentration of an alkane. Whether an alkane peak will show up in the chromatogram of a sulfur selective detector can be calculated from the concentration of the alkane in combination with the selectivity and sensitivity of the detector. In our study a sample volume of 100 mL is used as a safe upper limit.

When a large sample volume, e.g. 100 mL, is used, another important factor, the sampling flow rate, must be taken into consideration. During transfer of the loop contents into the liner, the adsorbent is purged with natural gas for a prolonged period. Due to the non-ideal behavior of natural gas the breakthrough volumes of the adsorbed sulfur species, especially of the most volatile ones H2S and COS, were found to strongly depend on the gas flow rate. It was found that with sampling flow rates up to approximately 50 mL/min, no component loss occurred. At higher sampling flow rates part of the adsorbed COS starts to break through. At a small sample volume, e.g. 13 mL, no effect of the sampling flow rate on the recovery was observed.

4 Conclusions

The ideal GC-based analytical instrument for sulfur determination in natural gas consists of three components: a selective (preferably on-line) sample pretreatment/enrichment device, a high resolution chromatographic column, and a sensitive, selective, and quenching-free detector. A programmed temperature vaporizing injector with a liner packed with the selective adsorbent Chromosorb 104 can act as an on-line sample enrichment device. The sulfur components from a large volume of natural gas are selectively collected while the hydrocarbons are either not retained or further eliminated by purging the liner with helium. The enriched sulfur components are then directly transferred to a 4 μm ultra-thick-film non-polar capillary column, and separated. The accuracy and precision of peak quantitation is further secured by employing a selective and sensitive sulfur detector, the SCD. With the proposed instrumental set-up equipped with a 13 mL sample loop, the detection limit achievable is appr. 3 μg S/m³. The accuracy and precision of the new method are, in general, better than 10% RSD. A good agreement between the new procedure and the standardized method was obtained for a limited set of test samples. The overall analysis time of the new method is about 30 min. The new method is clearly superior to the standardized method based on packed column GC-FPD without sample enrichment. With the latter technique, the risk of false positive identification is much larger. Moreover, quantitation is prone to errors by quenching or inaccurate calibration due to the non-linear calibration graphs. Lower detection and quantitation limits can be achieved by employing large sample volumes, either by larger sample loops or by direct sampling technique.

References


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