

Analysis of PFC Gas Tracers in Presence of High H₂S Concentrations

Perfluorocarbons (PFCs), used as gas tracers, can be detected down to femtogram amounts in petroleum reservoir gas matrices by applying Thermal Desorption in combination with GC/MS operated in the negative ion chemical ionization (NICI) mode.

INTRODUCTION

Hydrogen sulphide, often present in reservoir gases, deteriorate the analytical instrument performance rapidly when present in high concentrations, thus making the trace analysis unreliable or even impossible. This folder describes the successful use of a proprietary H₂S-scavenger, thus enabling the undisturbed tracer analysis even in gas matrices containing 50% hydrogen sulphide.

PFC TRACER ANALYSIS

PFC Tracers PDMCB PMCP PMCH 1,3-PDMCH

The reservoir gas samples are sampled on adsorption tubes, filled with 500 mg of a proprietary sorbent. When 20 ml gas sample is applied eluted through the tube, the PFC tracers are quantitatively adsorbed.

In the laboratory a thermal desorber transfers the analytes into a GC/MS system, operated in the NICI-mode. The method is capable to detect the PFC tracers in concentrations down to 10¹³ l/l (100 ppq)

INSTRUMENTATION

Thermal Desorber: PerkinElmer ATD 400
GC/MS: Agilent6890N/5973MSD
GC-column: J&W AI203/S 50 m x 0,32 ID x 8 μm

The analytical conditions are described in more detail elsewhere ^{1,2}.

ANALYSIS OF PFC WITHOUT H₂S

The Challenge

Low concentrations of H₂S in reservoir gas matrices do not normally present a problem for the established TD-GC/MS method. In some petroleum reservoirs however H₂S may be present at

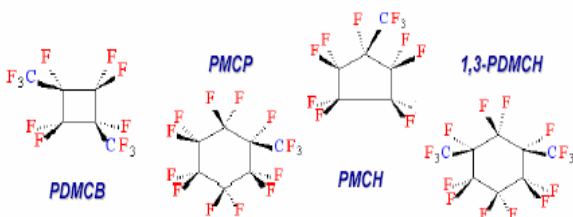


Figure 1. Structures of some typical PFC tracers: **PDMCB** (Perfluorodimethyl-cyclobutane), **PMCP** (Perfluoromethylcyclopentane), **PMCH** (Perfluoromethyl-cyclohexane), **1,3-PDMCH** (1,3-Perfluorodimethylcyclohexane)

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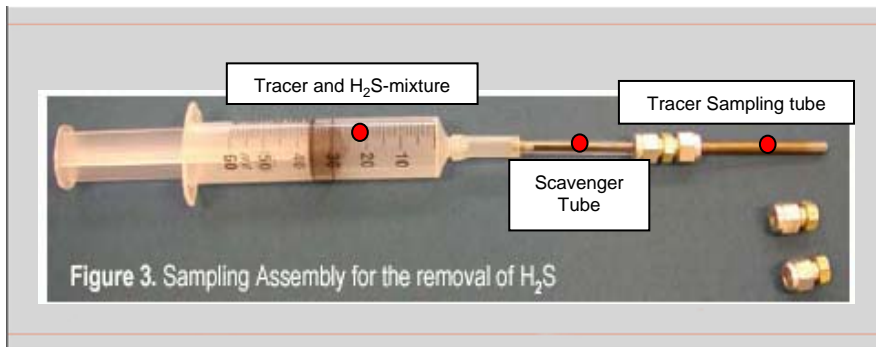
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CONCLUSIONS

A method for the removal of large amounts of H_2S in reservoir gas samples has been developed. The developed scavenger system removes the H_2S effectively while the PFC tracers are quantitatively recovered during this clean-up step.



concentrations as high as 50%. H_2S is to some extent trapped in the sampling tube, released and decomposed to elementary sulphur S_x during thermal desorption. S_x in turn adsorbs to the entire surface of the sample flow path of the instrumentation.

A high background signal of m/z 96 and 192, corresponding to S_3 and S_6 , was observed after the analysis of reservoir gas samples with high H_2S concentrations. The system performance deteriorated rapidly after only a few samples.

A complete exchange of all contaminated parts of the flow path and thoroughly cleaning of the ion source and the mass spectrometer was necessary to re-establish the usual instrument performance. Having also in mind the high costs of the long down-time of the instrumentation, it was very important to work out a procedure that could prevent such incidents to happen in the future.

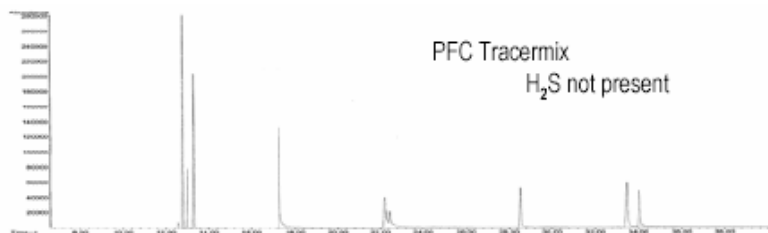


Figure 2. Total ion Chromatogram of a standard mix, without H_2S . Main peaks (in elution order): **PMCP**, 2 isomers of **PDMCB**, **PMCH**, **1,3-PDMCH** (cis/trans isomers and 1 contaminant), **PPCH** (Perfluoropropylcyclohexane) and the cis/trans isomers of **Perfluorodecaline**.

REMOVAL OF H_2S

To avoid H_2S from entering the instrumentation a “scavenger” tube was developed with a special filling material. The tube containing the H_2S scavenger was connected to the sampling tube as shown in Fig.3 above.

Natural gas containing 50% H_2S was directed with a gentle flow rate through the scavenger tube followed by flushing with clean air. As the gas entered the glass tube, the scavenger showed a color change. After sampling, about half of the scavenger material from the entry end along the tube had changed color, indicating that no (or very little) H_2S entered the tracer sampling tube. Other tests were made to confirm this observation.

ANALYSIS OF PFC AFTER H_2S REMOVAL

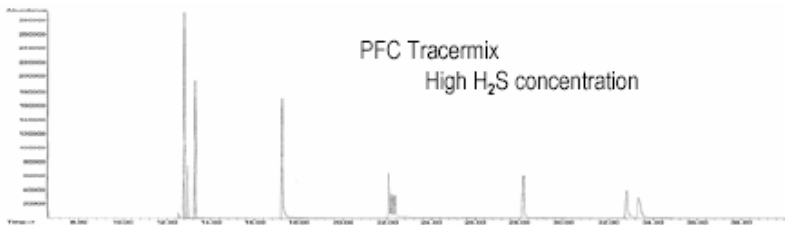


Figure 4. Total ion Chromatogram of a standard mix, containing large amounts of H_2S . Elution order as in Figure 2. The amount of tracers present in this sample is the same as in the sample shown in Figure 2. The retention times are slightly shorter and the peaks are somewhat broader than in the H_2S free sample. We assume that small amounts of H_2O present in the column, generated during the elimination of H_2S , are responsible for this effects. However the peak areas differ with less than 5 % compared to the H_2S -free sample, stating that the PFC tracers pass the scavenger quantitatively.