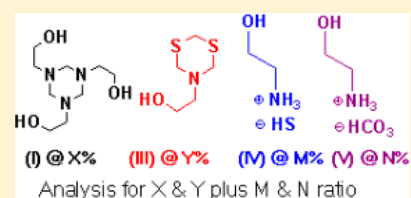


Use of Portable Analytical Methods to Determine the Stoichiometry of Reaction for Hexahydrotriazine-Based Hydrogen Sulfide Scavenger Operations

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ABSTRACT: During the reaction between 1,3,5-tris(2-hydroxyethyl)hexahydro-s-triazine and hydrogen sulphide, the principle by-product is the organic sulphide 5-(2-hydroxyethyl)dithiazine. It can be determined by a novel, portable, field-capable ion mobility spectrometry method described herein and enables the “degree spent” to be determined. Dependant upon the level of carbon dioxide in the produced gas, a mixture of ethanolaminium bicarbonate and ethanolamine bisulphide is also produced. Using a field capable spectrophotometric method the level of inorganic sulphide can be determined, thus allowing the ethanolaminium bisulphide concentration to be calculated. Provided the fluid is only partially spent, and there is some unreacted 1,3,5-tris(2-hydroxyethyl)hexahydro-s-triazine remaining; the only source of inorganic sulphide is the amine salt. From a knowledge of the original fluid concentration, the combination of these two methods allows the effective stoichiometry, or observed molar reaction proportions between 1,3,5-tris(2-hydroxyethyl)hexahydro-s-triazine and hydrogen sulphide, to be measured for a specific field location.



1,3,5-Tris(2-hydroxyethyl)hexahydro-s-triazine (I) or HHTT is a very widely occurring hydrogen sulfide scavenger. It reacts with hydrogen sulfide via the widely accepted reaction mechanism shown in Figure 1 to yield, as an exclusive product,

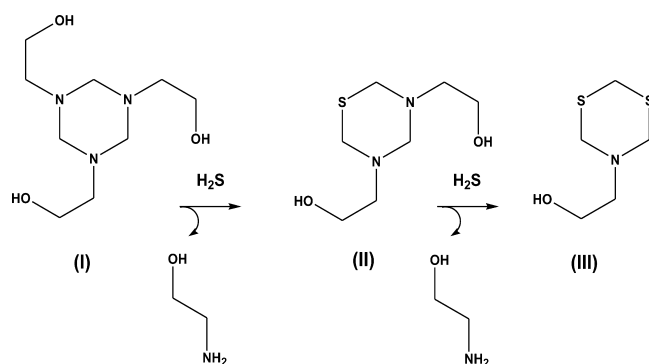


Figure 1. 1,3,5-Tris(2-hydroxyethyl)hexahydro-s-triazine reaction mechanism with hydrogen sulfide.

5-hydroxyethylhexahydrodithiazine (III) or DTZ. While the intermediate species 3,5-bis(2-hydroxyethyl)-hexahydrothiadiazine (II) must be a transient product, its presence has never been observed by a chromatographic method.

The analysis and properties of spent triazine hydrogen sulfide scavenger fluids has received a lot of attention recently. A laboratory method has been developed to determine the degree spent using chemical derivatization and gas chromatography.¹ While this method has been very useful and accurate it does require shipment of samples from the field and a relatively lengthy work-up and analysis. An improvement to the method used to remove water from the analytes was to azeotropically distill toluene from an aliquot of the aqueous spent fluid and

residue the solute with methylene chloride as a cosolvent prior to derivatization. It has been found that a convenient method to carry out this sample preparation is as follows. An aliquot (200 μL) of partially spent triazine based scavenger fluid is placed in a Reacti-Vial with stirrer. To this is added toluene (2 mL). The vial is placed in a heated and stirred Reacti-Block heater at 120 C. The rapid stirring prevents bumping and when the volume of toluene has been reduced by 50% to 1 mL all of the water has been removed by azeotropic distillation. The residue is then dissolved by the addition of methylene chloride (1 mL) followed by the derivatization agent, trifluoroacetic anhydride. After a period of stirrer to bring about complete solution the sample is ready to inject on to the GCMS. By means of this modified sample preparation method multiple samples can be prepared very quickly and efficiently. This improves the convenience and throughput for the existing “in house” method previously described.

Recently a mobile and potentially on site method has been described in the form of Field Asymmetric Ion Mobility Spectrometry (FAIMS).² This technique was developed ten years ago and has found wide applicability for a number of mobile analytical applications. Prior to the referenced study, however, the method had only been used for hydrocarbon media.³ It was recognized that this method had the potential to analyze aqueous fluids of a triazine origin and thus offer a field capable triazine scavenger based fluid analysis method. Using the FAIMS technique samples from the vapor head space of a heated sample are introduced into the analyzer using a stream

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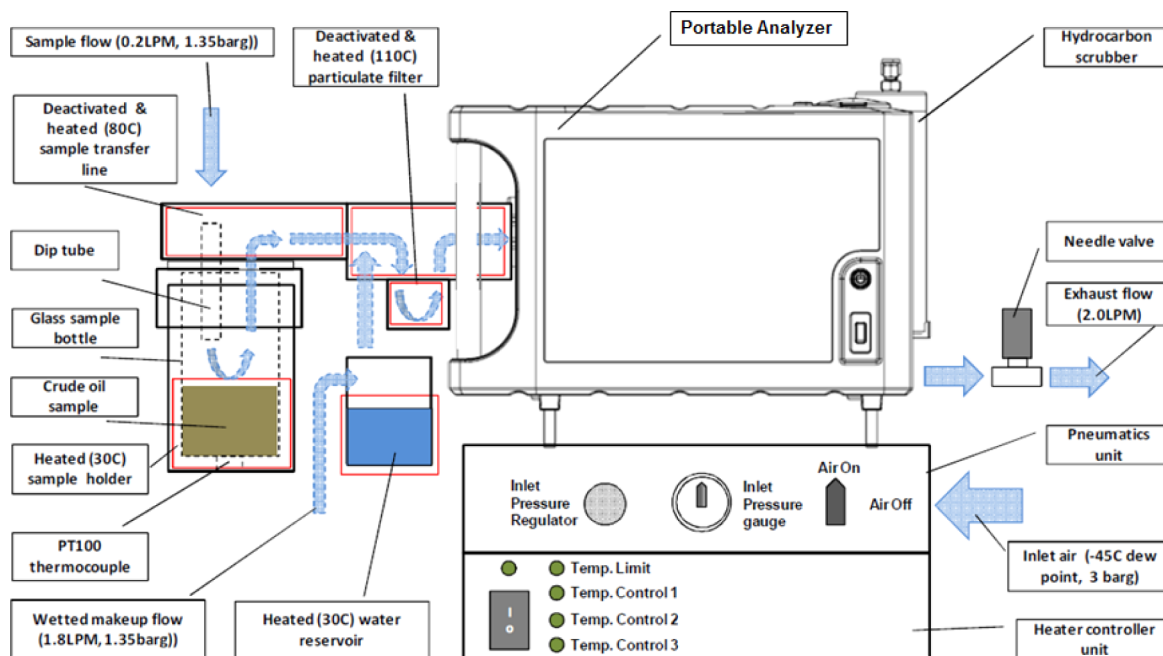


Figure 2. Schematic for Portable FAIMS Analyzer.

of purified carrier gas, typically air. A schematic of the portable analyzer is shown in Figure 2.

The analyte is vaporized and passes through the instrument through heated lines. A PC interface is used to control pressures and flow rates. When the vapor enters the portable analyzer it is ionized by a radioactive Ni-63 source beta emission source. Both positive and negative ions are formed. Ions enter the electrode channel where an RF waveform dispersion voltage (DV), applied to one electrode to create a varying electric field (dispersion field) under whose influence the ions follow different paths dependent on the ions' intrinsic mobility parameter. A DC compensation voltage (CV) is swept across the other electrode shifting the trajectories so different ions reach the detector, which simultaneously detects both positive and negative ions. The number of ions detected expressed as ion current is proportional to the concentration of the chemical in the sample.⁴

EXPERIMENTAL SECTION

A calibration response curve was determined for the two analytes (I) and (III). The application of this method was far from trivial and numerous problems were encountered. Pure (III), used in the calibration, was crystallized by purification from bulk spent field fluids gathered from field locations. Although spent triazine based field fluids are stable and do not degrade with time, it was found that aqueous solutions of pure (III) are unstable and have to be used within 24 h of their preparation. The response curve generated for (III) is shown in Figure 3.

It was also found that the presence of I reduced the FAIMS response of III and thus a correction factor response curve had to be developed that would overcome this complication and is shown in Figure 4.

The triazine (I) molecule is known to be readily hydrolyzed by acidic environments, and it was found to undergo certain degree of hydrolysis in the analyzer because of the protonic environment experienced the FAIMS instrument.⁵ Whenever pure I was introduced into the FAIMS instrument two peaks

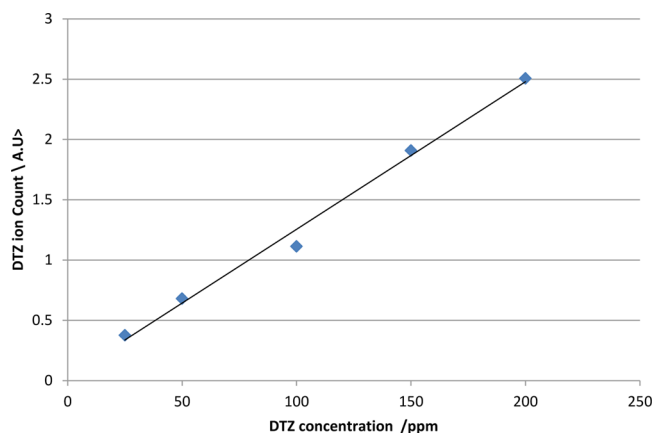


Figure 3. Dithiazine calibration curve at 90% dispersion field.

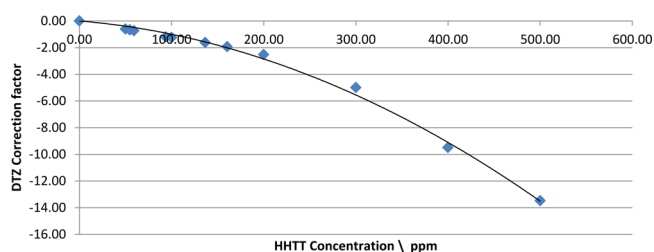


Figure 4. Correction factor to dithiazine concentration based upon HHTT concentration.

were observed in the response, the second being due to the presence of ethanolamine, the hydrolysis product of I under acid conditions. Knowing that one molecule of I yields 3 molecules of ethanolamine a suitable correction was made to the observed response to I to determine the concentration of I in the original sample. This was further complicated due to the fact that ethanolamine is also produced from the reaction of I with hydrogen sulfide (see Figure 1). The portion of ethanolamine from hydrolysis was calculated as a percentage

of the entire ethanolamine response from a knowledge the concentration of III in the fluid and the stoichiometry of reaction in Figure 1. By means of this correction method a calibration response with good linearity for I was determined and is shown in Figure 5.

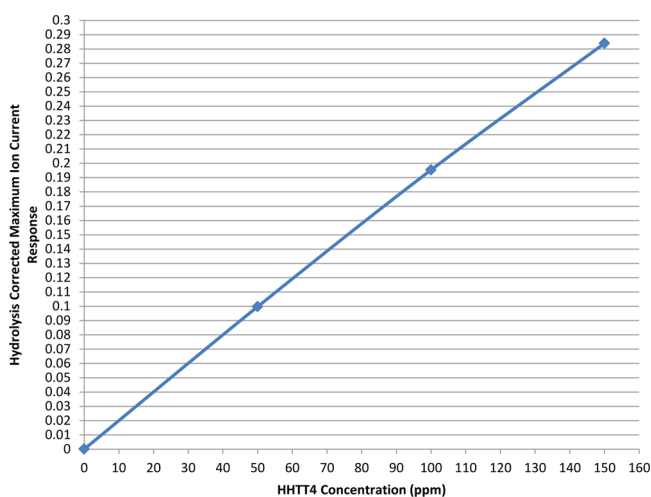


Figure 5. HHTT calibration curve at 90% dispersion field.

The FAIMS technique was used to determine the concentration of analytes (I) and (III) in an aqueous fluid directly with no need for extraction or chemical derivatization. The results have been compared with the previous in-house method requiring derivatization and GCMS analysis.¹ While the spent fluid is homogeneous it is quite stable. Some heavily spent field fluids were encountered. They have absorbed hydrogen sulfide to point whereby III either separates out as a crystalline solid or lower organic layer (depending on the temperature). This purified III very rapidly undergoes a polymeric reaction to yield amorphous dithiazine.⁶ When this happens the supernatant is severely depleted with respect to III. The comparative data for these two methods was found to have good agreement and is shown in Table 1.

It was concluded that it should be feasible to analyze the partially spent triazine based scavenger fluids for inorganic sulfide. Provided the scavenger is only partially spent the only source of inorganic sulfide would be ethanolaminium bisulfide (IV) or the salt of ethanolamine, liberated from the reaction of each mole of hydrogen sulfide with the triazine and subsequently the thiazine. The ethanolamine will also react with carbon dioxide in the system to form the ethanolaminium bicarbonate (V) as shown in Figure 6. There will be a competing reaction between carbon dioxide and hydrogen sulfide to salt the ethanolamine formed in the reaction.

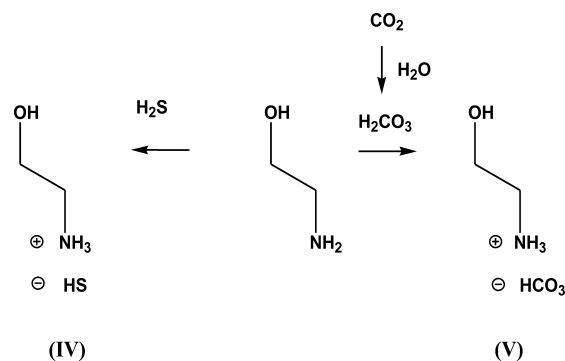


Figure 6. Ethanolamine salt formation.

A consideration of all the available methods for inorganic sulfide analysis revealed that the Hach DR 890 spectrophotometric technique with its hand-held colorimeter was the most suitable in this case.⁷ It relies upon to formation of methylene blue from the reaction of hydrogen sulfide with *N,N*-dimethyl-*p*-phenylenediamine oxalate as shown in Figure 7.

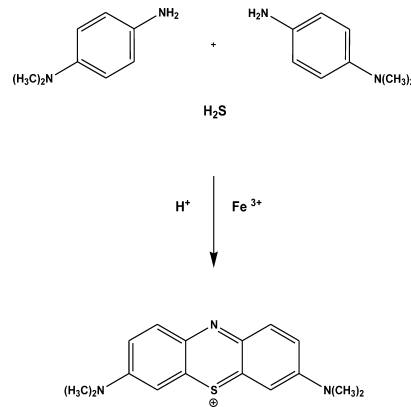


Figure 7. Reaction of *N,N*-dimethyl-*p*-phenylenediamine with hydrogen sulfide to form methylene blue.

The test sample is first acidified to convert all inorganic sulfide or bisulfide to hydrogen sulfide followed by reaction to form the intensely dark blue indicator which is then determined using a spectrophotometer, zeroed using a blank, and converted into inorganic sulfide concentration using the predetermined internal calibration. The maximum acceptable inorganic sulfide concentration for this method is 700 ppb and thus suitable dilutions were made prior to measurement. Before any determinations could be made however it was very important to confirm that the organic dithiazine (II) gave no response in this method. If there were any level of inorganic sulfide released into the system the method would be of no use. This was confirmed by measuring the absorbance of a solution of

Table 1. Field Sample Analysis by GCMS and FAIMS methodology

field sample	% hydrolysis	FAIMS HHTT (ppm)	FAIMS DTZ (ppm)	degree spent by FAIMS (%)	degree spent by GCMS ¹ (%)	solids
A	77.8	324 000	23 000	6.63		some amorphous dithiazine
B	80.0	50 000	1000	1.96		crystalline and amorphous solid
C	73.1	100 000	4800	4.58		lower liquid layer of dithiazine
D	83.1	222 000	21 300	8.75	12.2	no solid, homogeneous fluid
E	80.0	107 496	34 429	31.7	38.0	no solid, homogeneous fluid

Table 2. Calculated Stoichiometry of Reaction for I

field sample	triazine concentration (%)	degree spent (%)	determined % ethanolaminium bisulfide in fluid	calculated % ethanolamine reacting with hydrogen sulfide	calculated % ethanolamine reacting with carbon dioxide	calculated stoichiometry
A	22	38	0.7	9.9	90.1	2.20
B	44	6.63	2.05	81	19	3.62
C	44	10	1.95	52.2	47.8	3.04

dithiazine in water which would, if it were capable of total sulfide release, yield a solution of 1200 ppb inorganic sulfide, that is, double the maximum concentration for this method. The concentration of inorganic sulfide measured was 0.0 ppb, identical to the blank.

It was determined that analysis of spent triazine scavenger fluids offered the possibility to determine the concentration of ethanolaminium bisulfide and thus, by calculation, yield the proportion of ethanolamine that has reacted with hydrogen sulfide. From this value, it would be possible to calculate the ultimate total stoichiometry of reaction between triazine and hydrogen sulfide, a value between 2 and 4 depending upon the relative proportion of carbon dioxide and hydrogen sulfide in the system. Carbon dioxide significantly impacts the efficiency of triazine based hydrogen sulfide scavengers and an attempt has been made to study this in previous work.⁸

Partially spent triazine-based scavenger fluids, whose degree spent had already been determined by the FAIMS method, were analyzed using the Hach DR 890 spectrophotometric method 8131. The inorganic sulfide concentration was determined and for three field fluid samples. Assuming all inorganic sulfide comes from ethanolaminium bisulfide, the concentration of inorganic sulfide was converted into ethanolaminium bisulfide and expressed as a percentage of the total salted ethanolamine in the system. The theoretical stoichiometry value of 2 for reaction of acid gases with ethanolamine is shared between carbon dioxide and hydrogen sulfide. This percentage gives the proportion that has reacted with hydrogen sulfide and thus when combine with the stoichiometry of reaction to itself the dithiazine, gives the overall stoichiometry of reaction with hydrogen sulfide. This will be a value between 2 and 4, closer to 2 in high carbon dioxide environments and closer to 4 where there is little of no carbon dioxide. The calculated stoichiometry of reaction determined and shown in Table 2.

CONCLUSION

The exact stoichiometry of reaction is not an easy parameter to accurately measure. In conditions of high carbon dioxide levels, often significantly higher than the hydrogen sulfide content, it is often assumed to be 2 since it is assumed none of the ethanolamine will react with hydrogen sulfide. Under conditions where this is not the case, the method offers a way to calculate this important parameter and allow more accurate calculation of volume requirements and residence times for dynamic and static gas scrubber towers.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

REFERENCES

(1) Taylor, G. N.; Matherly, R. *Ind. Eng. Chem. Res.* **2010**, *49*, 6267–6269.

(2) Wilks, A.; Hart, M.; Koehl, A.; Somerville, J.; Boyle, B.; Ruiz-Alonso, D. *Int. J. Ion Mobility Spectrom.* **2014**, *15* (3), 199–222.

(3) Boyle, B.; Freshman, S. *Lonestar Hydrogen Sulfide Scavenger Analyzer. Rapid, At-Line Analysis of Hydrogen Sulfide Scavenger and By-Products in Crude Oil Using Lonestar*, Owlstone White Paper; Owlstone: Norwalk, CT, 2013.

(4) Taylor, G. N.; Matherly, R. *2013 SPE Oilfield Chemistry Symposium —The Evaluation and Optimization of Hydrogen Sulfide Scavenger Applications Using Ion Mobility Spectrometry*, SPE 164133; Baker Hughes Company, Tomball, TX, 2013.

(5) Bakke, J. M.; Buhaug, J.; Riha, J. *Ind. Eng. Chem. Res.* **2001**, *40*, 6051–6054.

(6) Taylor, G. N.; Matherly, R. *Ind. Eng. Chem. Res.* **2011**, *50*, 735–740.

(7) U.S. EPA Method 376.2 or Standard Method 4500-S²-D for wastewater.

(8) Taylor, G. N. and Matherly, R. *The Laboratory Evaluation and Optimization of Hydrogen Sulfide Scavengers Using Sulphur Specific Flame Photometric Gas Chromatography*, 2011 SPE Oilfield Chemistry Symposium, SPE 140401; B.J.Services, Chemical Services: Tomball, TX, 2011; 77375.