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**INSTRUMENTAL METHODS OF ANALYSIS OF SULFUR
COMPOUNDS IN SYNFUEL PROCESS STREAMS**

Quarterly Technical Progress Report for the Period April—June 1984

By
Joseph Jordan
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Work Performed Under Contract No. FG22-81PC40783

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INSTRUMENTAL METHODS OF ANALYSIS OF SULFUR
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for the period
April - June 1984

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ABSTRACT

TASK 1. METHODS DEVELOPMENT FOR THE SPECIATION OF THE POLYSULFIDES. Work on this task has been completed in December 1983 and reported accordingly in DOE/PC/40783-T13.

TASK 2. METHODS DEVELOPMENT FOR THE SPECIATION OF DITHIONITE AND POLYTHIONATES. Electrochemical reduction of tetrathionate and pentathionate at the dropping mercury electrode (DME) proceeds through a mechanism involving specific adsorption of the reactant at the DME surface and yielding polarographic waves at -0.2 volt (versus the saturated calomel electrode) in aqueous solution. Ethanol interferes with the specific adsorption of tetrathionate and pentathionate in a range of potentials between 0.0 and -1.1 volt, because EtOH is preferentially adsorbed. This results in a shift of the polarographic half-wave potentials of tetrathionate and pentathionate, which facilitates their determination in polythionate mixtures. On the other hand, the polarographic reduction of trithionate is unaffected by ethanol, because it occurs at -1.5 volt where ethanol is not adsorbed at the surface of the DME.

TASK 3. TOTAL ACCOUNTING OF THE SULFUR BALANCE IN REPRESENTATIVE SAMPLES OF SYNFUEL PROCESS STREAMS. Analyses of two aqueous gasifier effluents from Grand Forks, ND, were performed. An untreated specimen contained sulfidic and polysulfidic sulfur, thiosulfate and thiocyanate. On the other hand, sulfite, sulfate, and thiocyanate were the only sulfur moieties observed in the Grand Forks sample which had been stripped at PETC.

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OBJECTIVE AND SCOPE OF WORK

The general objective is to develop dependable and accurate instrumental analysis methods for the determination of sulfur moieties. These will include polysulfides, dithionite and polythionates. Calorimetric procedures (thermo-metric titrations, injection enthalpimetry) and electroanalytical techniques (voltammetry, coulometric analysis, etc.) will be used. The complete speciation of sulfur will be undertaken in representative synfuel process stream samples.

TASK DESCRIPTIONS

TASK 1. METHODS DEVELOPMENT FOR THE SPECIATION OF POLYSULFIDES.

Thermochemical and electrochemical methods of analysis will be developed for the determination of $S^=$, $S_2^=$, $S_3^=$, $S_4^=$, $S_5^=$, and of higher polysulfides if applicable.

TASK 2. METHODS DEVELOPMENT FOR THE SPECIATION OF DITHIONITE AND POLYTHIONATES.

Electroanalytical and/or thermochemical methods of analysis will be developed for the determination of $S_2O_4^=$, $S_2O_6^=$, $S_3O_6^=$, $S_4O_6^=$, $S_5O_6^=$, $S_6O_6^=$, and of higher polythionates.

TASK 3. TOTAL ACCOUNTING OF THE SULFUR BALANCE IN REPRESENTATIVE SAMPLES OF SYNFUEL PROCESS STREAMS.

Diverse samples will be analyzed. The results will be intercompared critically and "fingerprint features" of sulfur distribution (between various oxidation states and conjugate Bronsted acid-base moieties, etc.) will be correlated to type of coals, methods and conditions of conversion and other significant variables.

PROGRESS REPORT CHART

Task	1981	1982				1983				1984		
	Oct. - Dec.	Jan. - March	Apr. - June	July - Sept.	Oct. - Dec.	Jan. - March	Apr. - June	July - Sept.	Oct. - Dec.	Jan. - March	Apr. - June	July - Sept.
1) Methods Development for the Speciation of the Polysulfides.												
2) Methods Development for the Speciation of Dithionite and the Polythionates.												
3) Total Accounting of the "Sulfur Balance" in Representative Samples of Synfuel Process Streams

Scheduled

Scheduled Extension

Progress

Early Start

SUMMARY OF PROGRESS TO DATE

This is the eleventh quarterly report on work performed under Grant DE-FG22-81PC40783, initiated on September 30, 1981.

TASK 1. METHODS DEVELOPMENT FOR THE SPECIATION OF THE POLYSULFIDES. The Lewis acid p-hydroxymercuribenzoate (HMB) has been found to be a valuable reagent for the determination of polysulfides by thermometric titration. Titration of a solution containing both hydrosulfide (HS^-) and polysulfides (S_x^{2-} , $2 < x < 5$) has yielded two discrete endpoints. The first endpoint corresponds to hydrosulfide and the second to twice the molar-sum of hydrosulfide plus polysulfides. The average chain length of the polysulfides has been found to be dependent on pH. The trimetrically determined average chain length at pH 14 is four, corresponding to a rearrangement of both trisulfide and pentasulfide to tetrasulfide. The reactions of thiosulfate, cyanide, iodide, sulfite, ammonia and thiocyanate with HMB have been investigated and assignments made for the enthalpies and Gibbs free energy of reaction. The reagent p-HMB is characterized as an adduct of the strong, soft Lewis acid $^-\text{OOC}_6\text{Hg}^+$ and the hard base hydroxide. On the other hand, thallium (I) is a soft Lewis acid which is selective for sulfide and polysulfide moieties as a group but lacks the specificity to distinguish between HS^- and individual polysulfides. An electrochemical technique has been developed to determine polysulfidic sulfur by polarography at the dropping mercury electrode. Electrode reactions of the type

are implicated. The method is applicable to a range of concentrations between 5×10^{-5} and 3×10^{-3} M. For the determination of "sulfidic sulfur

$$[\text{HS}^-] + \sum_{x=2}^5 [\text{S}_x^{2-}]$$

advantage was taken of diffusion currents corresponding to the following anodic depolarization reactions of the dropping mercury electrode:

which overlap in a range of potentials between -0.65 and +0.2 volt versus the saturated calomel electrode.

NOTE: WORK ON TASK 1 WAS COMPLETED IN DECEMBER 1983 AND IS REPORTED IN DOE/PC/40183 T10-14.

TASK 2. METHODS DEVELOPMENT FOR THE SPECIATION OF DITHIONITE AND THE POLYTHIONATES. The literature on the electroreduction and electrooxidation of dithionite, trithionate, tetrathionate and pentathionate has been reviewed previously. Dithionite appears to be electrochemically inert. However, a wealth of information is available on electroreduction processes which are likely to yield cathodic current-voltage curves amenable for analytical utilizations. Thus trithionate is known to be electroreduced to a mixture of sulfite and thiosulfate, where as tetrathionate yields thiosulfate as its sole electroreduction product. It has been reported that pentathionate is electroreducible to a mixture of thiosulfate and elemental sulfur and dithionite yields sulfoxylate (SO_2^-) upon electroreduction. A few electrooxidation reactions of the relevant moieties have also been reported, yielding corresponding anodic current-voltage curves. Experimentally, it has been found that trithionate, tetrathionate, pentathionate, and hexathionate indeed yielded well defined polarographic electroreduction waves at the dropping mercury electrode. A polarographic procedure has been developed for the determination of tetrathionate and pentathionate in the presence of each other. The method is based on measuring diffusion currents (at the dropping mercury electrode) at two discrete potentials where the following electrode reactions occur:

It has been found that trithionate, tetrathionate, and pentathionate yield well-resolved differential pulse polarographic peaks at the dropping mercury electrode using a mixed solvent of 60% water/40% ethanol (v/v). Polythionate speciation is feasible without prior separation. Remarkably, the polarographic half-wave potential of the reduction of tetrathionate (to thiosulfate) is shifted by -1.1 volt when the solvent is changed from pure water to an ethanol-water mixture. Concomitantly ethanol is adsorbed at the electrode interface. However, the principal overall electroreduction stoichiometries of the polythionates are the same in the presence and in the absence of ethanol, viz.,

Furthermore, tetrathionate, pentathionate, and hexathionate were found to be electrooxidable at glassy carbon anodes, while trithionate was not. The heat of oxidation-reduction reactions of the type

and of the cyanolysis reactions

have been identified as promising starting points for the development of instrumental methods for the determination of polythionates.

TASK 3. TOTAL ACCOUNTING OF THE SULFUR BALANCE IN REPRESENTATIVE SAMPLES OF SYN FUEL PROCESS STREAMS. Inquiries have been sent to industrial, government, and academic organizations, soliciting appropriate specimens. Responses have been received from more than a dozen individuals, who have access to diverse samples in various locations, ranging from Washington, Oregon, and California to New York, Delaware, and the Carolinas. ** Specimens were stored in a nitrogen dry-box facility. Its effectiveness in minimizing sample oxidation was verified by duplicate analysis of two H-Coal® sour water samples which had been so stored for over two years. ** A five-step protocol has been formulated for speciating and quantitating the major and minor moieties which contribute to the total sulfur content. Analysis of polysulfides in H-Coal sour water samples yielded comparable results by electrochemical, thermochemical, and classical methods. ** A gasifier condensate was found to contain no sulfide, polysulfides, or thiosulfate by any method. An SRC-II aqueous effluent was found to contain some thiosulfate by both electrochemical and thermochemical methods. ** Analysis of aqueous H-Coal liquefaction process effluent sample by electroanalytical and thermochemical methods showed that the predominant sulfur species was HS⁻. Polysulfides were present in aged specimens. ** In contrast, an aqueous gasification effluent sample from Grand Forks, ND, contained not only sulfidic and polysulfidic sulfur but also thiosulfate and thiocyanate. ** Liquefaction (SRC process) samples from the pilot plant at Wilsonville, Alabama, taken from different stages in the wastewater treatment were found to contain sulfate and thiosulfate. ** A liquefaction sample from PETC's Disposable Catalyst Development (DCD) unit contained a mixture of sulfide and polysulfides. ** Two H-Coal liquefaction effluents originating from the pilot plant at Catlettsburg, Kentucky, were treated at PETC. These wastewater samples were obtained from different stages of the PETC clean-up treatment and both contained comparatively low concentrations of sulfur which consisted predominantly of sulfate. ** Two aqueous effluents from different stages in the CE LUMMUS liquefaction unit in New Brunswick, NJ were analyzed. Total sulfur content was in a range between 0.0006 M and 0.0010 M which was too low for speciation of the various sulfur moieties. ** Two aqueous specimens originating from the gasification unit in Grand Forks, North Dakota, contained thiocyanate. Sulfide, polysulfides, and thiosulfate were observed in an untreated

effluent sample but were absent in a sample which had been stripped at PETC. Sulfur and sulfate were also present in the stripped specimen. **

DESCRIPTION OF TECHNICAL PROGRESS

TASK 1. METHODS DEVELOPMENT FOR THE SPECIATION OF THE POLYSULFIDES

Work on this task has been completed¹ on December 31, 1983. A summary of accomplishments is given on page 5 above. An appropriate synopsis will be included in the Final Technical Report in September 1984.

TASK 2. METHODS DEVELOPMENT FOR THE SPECIATION OF DITHIONITE AND POLYTHIONATES

As has been previously reported^{1,2,3}, the presence of 40 volume percent ethanol has drastic effects on the polarography of tetrathionate and pentathionate (as compared to their polarography in an aqueous supporting electrolyte and in the absence of ethanol). The nature of these effects is apparent from Figure 2.1, viz.,

- (a) The half-wave potential of $S_4O_6^{2-}$ undergoes a very large negative shift (1.1 volt).
- (b) In lieu of the two well-defined waves observed in aqueous solution, $S_5O_6^{2-}$ yields only a single well-defined wave plus two ill-defined prewaves.

Ethanol was adsorbed at the dropping mercury electrode surface in the potential domain identified in Figure 2.1. A theoretical explanation was inferred during the current quarterly period. The relevant rationale is summarized below.

The observed currents are accounted for as follows:

The overall reaction stoichiometries of Equations 2.1 and 2.2 are the same in the presence and absence of ethanol. The shift of the half-wave potential of Reaction 2.2 is due to the fact that electroreduction of $S_4O_6^{2-}$ appears to be contingent on its prior specific adsorption at the electrode surface, viz.,

Figure 2.1

Comparison of Polarograms of Polythionates at the Dropping Mercury Electrode (DME) in Pure Water and in a Mixed Water-Ethanol Solvent. Supporting electrolyte: phosphate buffer, pH 6.5. Concentration of polythionates $\approx 10^{-4}$ Molar. Potential scanned cathodically from 0.0 to -1.8 volt vs SCE.

The sequence of Reactions 2.3, 2.4, 2.5 represents the mechanism of Reaction 2.2 regardless of the presence or absence of ethanol. The potential determining step is Reaction 2.4. The corresponding half-wave potential is -0.20 volt versus SCE which is indeed observed in the absence of ethanol where Reaction 2.3 can readily occur. On the other hand, ethanol which is very strongly adsorbed between -0.0 volt and -1.1 volt, "blocks" the electrode surface thus preventing Reaction 2.3 and consequently Reactions 2.4 and 2.5 as well. If potentials are scanned cathodically (as in Figure 2.1), Reactions 2.3, 2.4, 2.5 cannot take place until ethanol is desorbed at -1.1 volt, where indeed the tetrathionate wave was observed in the presence of ethanol.

The reduction of trithionate is unaffected by the presence of ethanol because it reduces at -1.50 volt where ethanol is never adsorbed on the mercury indicator electrode.

As far as the behavior of pentathionate is concerned, we postulate that it occurs via the following chemical-electrochemical-electrochemical (CEE) sequence.

The sequence of Reactions 2.6 through 2.9 adds up to Reaction 2.12, viz.,

which accounts for Wave I in Figure 2.1. Wave II corresponds to Reaction 2.10 + Reaction 2.11, i.e.,

The value of the limiting current of Wave II is accounted for by the summations of Reactions 2.6 through 2.11, which is the same as Reaction 2.12 + Reaction 2.13, viz.,

The potential determining step of Reactions 2.12 and 2.13 is Reactions 2.8 and 2.10 respectively. The corresponding half-wave potentials are:

$$E_{\frac{1}{2}}^{2.8} = -0.20 \text{ v} \quad (2.15)$$

$$E_{\frac{1}{2}}^{2.10} = -0.59 \text{ v} \quad (2.16)$$

In the absence of ethanol the initial step (Reaction 2.6) can readily occur at these potentials and Wave I (Reaction 2.12) and Wave II (Reaction 2.13) are observed accordingly.

When ethanol is adsorbed (at potentials between 0.0 and -1.1 volt from a mixed solvent of 60% H₂O - 40% EtOH), the initial Reaction 2.6 is inhibited and Waves I and II decrease to two small prewaves as seen in Figure 2.1. At the potential where ethanol again desorbs ($E < -1.1$ volt) a wave corresponding to Reaction 2.14 is obtained. Thus the electroreduction of pentathionate of the DME yields two discrete two-electron waves in the absence of ethanol (I and II in Figure 2.1). These are replaced by a single four-electron wave (III in Figure 2.1) in the presence of ethanol.

TASK 3. TOTAL ACCOUNTING OF THE SULFUR BALANCE IN REPRESENTATIVE SAMPLES OF SYN FUEL PROCESS STREAMS

Two aqueous effluents from the gasification unit in Grand Forks, ND, were analyzed this quarter. A description of the samples and their storage before arrival at Penn State is given in Table 3.1. Following the protocol outlined previously⁵, the total sulfur, redox potential, and pH of the samples were determined, as reported in Table 3.2. Results of sulfur speciation analyses are reported in Table 3.3.

Table 3.1

Description of Samples of Synfuel Process Streams

Identification	G-3	G-4
Supplier	J. Hendrikson Univ. of ND Energy Research Center (UNDERC) Box 8213 Grand Forks, ND 58202	C. Drummond DOE, PETC Pittsburgh, PA 15236
Description	Aqueous effluent of slagging fixed bed gasifier; Grand Forks, ND, plant; North Dakota lignite processed August 1983	G-2 after stripping treatment at PETC ^{1,3}
Storage before arrival at Penn State	Sealed in polyethylene bottle	Sealed in polyethylene bottle

Table 3.2

Characterization of Aqueous Coal Conversion Process Stream Specimens

(1) <u>Identification</u> ^(a)	(2) <u>Description</u>	(3) <u>pH</u>	(4) <u>Redox Potential</u> ^(b)	(5) <u>Total Sulfur</u> ^(c)
G-3	Gasifier effluent	8.5	-0.18	0.0166±0.0008
G-4	"Stripped" gasifier effluent	7.3	+0.20	0.0092±0.0006

(a) See Table 3.1

(b) Volt versus Normal Hydrogen Electrode

(c) Moles sulfur per liter

Table 3.3

Summary of Results of Determination of Sulfur Moieties in Synfuel Process Stream Samples^(a)

Concentrations (millimole·L ⁻¹)	Sample G-3		Sample G-4	
	<u>Method</u>		<u>Method</u>	
	Thermochemical	Electrochemical	Thermochemical	Electrochemical
Sulfidic S(-II)	10.2	9.0	<0.2 ^(b)	<0.5 ^(b)
Polysulfidic S(0)	3.	2.	<0.2 ^(b)	<0.5 ^(b)
Thiosulfate	NA	0.2	<0.2 ^(b)	<0.2 ^(b)
Sulfite	NA	<0.2 ^(b)	NA	1.7
Sulfate	NA	NA	<2.0	NA
Thiocyanate	8 ^(c)	Present	1.7	Present

(a) See Table 3.1 for identification

(b) Detection limit

(c) Rough estimate

NA = Not available

ANALYSIS OF GRAND FORKS SPECIMEN, G-3, using thermochemical and electrochemical methods yielded good agreement for the predominant sulfur moiety, sulfidic sulfur, and fair agreement for polysulfidic sulfur (Table 3.3). Thiocyanate was also detected by both methods as follows.

- (a) Electrochemically: the presence of thiocyanate was recognized by its characteristic anodic depolarization potential (+0.18 volt versus SCE) at the dropping mercury electrode.
- (b) Enthalpimetrically: presence of thiocyanate was inferred from thermometric titration curves.

The titrant was a standard solution of silver nitrate, which reacted with thiocyanate:

Titration curves of the effluent specimen were intercompared with titration curves of an aliquot doped by a standard addition of potassium thiocyanate. In this manner a semiquantitative rough estimate of 0.008 M was obtained for the thiocyanate content of the effluent. Similar specimens are known to contain thiocyanate in a range of concentrations between 3 and 7 millimolar⁶. The total sulfur content of specimen G-3 (Table 3.2) is consistent with a thiocyanate concentration of 0.004 M, which corresponds to the middle of this range. Thus it appears that the thermochemical estimate of 0.008 M thiocyanate may have been high by a factor of two. A small amount (0.0002 M) of thiosulfate was also detected in sample G-3 (electrochemically).

Analysis of a raw (untreated) effluent (G-2)¹ from a previous run of the Grand Forks gasifier has been performed and a comparison of the results of G-3 with this sample is appropriate. The total sulfur and pH for G-2 were 15.3 millimolar and 8 to 9 respectively. Although G-3 was obtained from a later batch, the total sulfur and pH of G-3 (16.6 millimolar and 8.5, respectively) are comparable to the analogous data for G-2. Sulfidic, polysulfidic sulfur, thiosulfate, and thiocyanate were all detected in both specimens. Sulfidic sulfur was observed to be much lower in G-2 (2.1 millimolar) than in G-3 (Table 3.3). Polysulfidic sulfur results for G-2 and G-3 (1.4 millimolar and 2 to 3 millimolar, respectively) are comparable. Finally thiosulfate was detected at a much lower concentration in G-3 than in G-2 (0.2 versus 2.0 millimolar, respectively). Variations in sulfur speciation data may be explained by differences in batch operating conditions, such as sample storage, etc.

ANALYSIS OF THE STRIPPED GRAND FORKS SAMPLE, G-4, via thermometric and electrochemical techniques yielded no detectable sulfidic sulfur, polysulfidic sulfur, or thiosulfate. Sulfite was measured electrochemically at 1.7 millimolar and thiocyanate thermochemically at the same concentration. Last, sulfate was calorimetrically observed but for reasons previously described⁷, not quantified. The sum of all the moieties (quantified electrochemically and thermochemically) accounts for 0.006 M sulfur at most. This is at variance with the total sulfur determined, viz., 0.009 M. The discrepancy, which we cannot explain, is puzzling.

As sample G-4 is actually G-2 which has been stripped at PETC, comparison of G-4 and G-2 may be enlightening. The PETC stripping procedure has been described elsewhere³. It could reasonably be anticipated that sulfidic sulfur and polysulfidic sulfur content would be greatly reduced by the stripping procedure. This indeed was the experimental finding. The pH of G-2 was in a range between 8 and 9, while G-4 had a pH of 7.4. This decrease in basicity is accounted for by the removal of ammonia in the stripping process. Another comparison of these two samples reveals that thiocyanate was present in both. This finding is reasonable because thiocyanate content is not affected by the PETC stripping procedure.

CONCLUSIONS

TASK 2. METHODS DEVELOPMENT FOR THE SPECIATION OF DITHIONITE AND AND POLYTHIONATES. The adsorption of ethanol at the surface of the dropping mercury electrode is instrumental in separating the polarographic waves of pentathionate and tetrathionate which overlap in the absence of ethanol. This provides the rationale for using a water-ethanol solvent mixture in the polarographic speciation and determination of polythionates present in mixtures.

TASK 3. TOTAL ACCOUNTING OF THE SULFUR BALANCE IN REPRESENTATIVE SAMPLES OF SYN FUEL PROCESS STREAMS. The most obvious conclusion that can be inferred from the analysis of specimens G-3 and G-4 is that a dependable quantitative method of thiocyanate analysis is needed in order to achieve a total accounting of the sulfur balance in these process streams. Since the presence of thiocyanate was initially observed in G-2, work has been in progress to develop a thermometric method of analysis for this anion.

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