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Gas Analysis Procedures Applicable to Flue Gas Desulfurization by the Citrate Process

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GAS ANALYSIS PROCEDURES APPLICABLE TO FLUE GAS DESULFURIZATION BY THE CITRATE PROCESS

by

H. R. Beard,[1] K. R. Farley,[2] S. R. Crane,[3] and W. N. Marchant[1]

ABSTRACT

The citrate process for sulfur dioxide emission control was developed in pursuit of the Bureau of Mines goal of minimizing the adverse environmental impact of mineral-processing operations. This publication describes the gas analysis procedures used during development of the process. The research required the capability to analyze SO_2, H_2S, CO, CO_2, COS, volatile hydrocarbons, NO, NO_2, O_2, N_2, and H_2. The methods described include gas chromatography, electrochemical detection, infrared spectroscopy, and the use of a computer program to predict the product composition in complex reactions. Laboratory and pilot plant applications are discussed.

INTRODUCTION

One of the Bureau of Mines goals is to minimize the impact of mineral-processing operations upon the environment. Accordingly, development of effective pollution control procedures is an integral part of the Bureau's metallurgy research program. The citrate process for SO_2 emission control is a product of this research (4).[4]

Briefly, the citrate process comprises three steps. First, SO_2 is absorbed from a cleaned and cooled waste-gas stream into a solution of citric acid and sodium citrate. Citrate buffers the absorber solution against the pH decrease that would otherwise accompany SO_2 dissolution and severely limit its solubility. Second, the absorber solution containing dissolved SO_2 is reacted with gaseous H_2S to produce elemental sulfur. Hydrogen sulfide for this step is produced in a separate unit operation by reacting elemental sulfur with steam and a reducing agent (natural gas, carbon monoxide, methanol, coal, etc.) at about 650° C. Finally sulfur is separated from regenerated

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[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

absorbent solution by flotation. The float product is subsequently separated from entrained absorbent by autoclave heating to about 135° C, which melts the sulfur, forming a lower liquid phase from which absorbent solution comprising the upper phase is withdrawn for recycle. Part of the molten sulfur is diverted to the H_2S-generator section, and the balance is cast into blocks for storage, sale or other use.

To support laboratory and pilot plant tests and to insure safety in the experimental environment, it was essential to be able to detect and quantify all gases that are either reactants or products in the process. This paper describes the gas analysis procedures used during citrate process development and testing, and provides a single source of information about these procedures for reference by other users of gas desulfurization technology.

SCOPE

In the principal citrate process operation, SO_2 dissolved in citrate absorbent is treated with gaseous H_2S to produce elemental sulfur; however, in process operation, pure gaseous H_2S and SO_2 rarely occur. Furthermore, H_2S generation produces minor amounts of other gases that must be identified. Thus, research requirements included the capability to analyze oxygen, nitrogen, hydrogen, and the following gases, often in complex mixtures:

1. Sulfur dioxide (SO_2)
2. Hydrogen sulfide (H_2S)
3. Carbon monoxide (CO)
4. Carbon dioxide (CO_2)
5. Carbonyl sulfide (COS)
6. Volatile hydrocarbons (natural gas components)
7. Nitrogen dioxide (NO_2)
8. Nitric oxide (NO)

Because some of these gases are hazardous, methods for detecting leaks and alerting project personnel are essential, and are described herein.

Gases subject to analysis varied greatly in composition, but they may be described in three broad classes as follows:

1. SO_2-containing gases. These included both laboratory-synthesized mixtures that ranged from 100 percent SO_2 to a few parts per million (ppm) of SO_2 in nitrogen diluent, and pilot plant feed gas that contained about 0.5 pct SO_2 plus 5 to 10 pct CO_2 in air.

2. H_2S-containing gases. In the laboratory, these consisted of H_2S in commercial cylinders at concentrations between 100 pct and about 10 pct diluted with nitrogen. Hydrogen sulfide generated in process simulations or at the Bunker Hill pilot plant contained, typically, 76 pct H_2S, 18 pct CO_2, 3 pct methane, 1 pct N, 1.5 pct COS, and lesser amounts of CS_2 and O_2.

3. Miscellaneous gases, including natural gas. These typically consisted of 90 pct methane, 5 pct ethane, 1 pct CO_2, lesser amounts of C_3-C_7 hydrocarbons, and 3 to 30 ppm sulfur from naturally occurring H_2S plus sulfur-containing odorants added by the distributors. In some laboratory experiments, nitrogen oxides were added either singly or in combination to the simulated waste gas at concentrations of 50 to 200 ppm for NO_2 and 500 to 2,000 ppm for NO.

During process development, both qualitative and quantitative analyses were required. The techniques used include gas chromatography (GC), infrared absorption spectroscopy (IR), electrical conductivity measurement, electrochemical and flame photometric detection, and chemical tests. In addition, a computer program for predicting the product gas composition in complex reactions was used to detect potential toxic constituents of process gas streams.

The analyses most frequently required were for control of laboratory or pilot plant experimental conditions rather than ambient air monitoring. For this reason, some techniques were capable of greater sensitivity than was used in the application described. Where a procedure can be modified to achieve greater sensitivity, as might be necessary to monitor concentrations near the threshold limit value (TLV), this will be noted.

QUALITATIVE ANALYSIS--GAS DETECTION

Both SO_2 and H_2S are easily recognized by their distinctive odors; however, both gases are toxic and detection by odor alone is not an adequate personnel safeguard. Furthermore, exposure to even low concentrations of H_2S desensitizes the olfactory response so that odor is a totally unreliable indicator for H_2S (2). For these reasons, sensitive, reliable detection methods must be available to personnel working with these gases.

Three methods were used for H_2S detection in the test environment. A Bacharach Instrument Co. continuous air-monitoring system[5] was provided for both process investigation unit experiments at the Salt Lake City (Utah) Metallurgy Research Center and pilot plant tests at the Bunker Hill lead smelter at Kellogg, Idaho. This system included remote electrochemical sensors strategically located in the test area and coupled to a central control panel. Within each sensor is a proprietary, solid-state element that undergoes a reversible reaction with H_2S. This produces a change in resistivity that is translated by means of an impedance matching circuit into a current proportional to the H_2S concentration. Each sensor functions independently, and, at H_2S concentrations exceeding 10 ppm, actuates an alarm easily audible above

[5]Reference to specific companies or brand names is made for identification only and does not imply endorsement by the Bureau of Mines.

background noise. In addition to this fixed installation, a battery-powered, portable detector operating on the same principle was used in laboratory tests. This instrument could be placed immediately adjacent to a test area, insuring continuous air monitoring.

Rapid routine checks for H_2S were made with moistened lead acetate paper (5). Commercially available paper test strips are convenient for local tests, as in a leak check, and may be used in locations where equipment configuration prevents accurate positioning of an electrochemical sensor. Such strips show a marked color change from white to brown-black in the presence of H_2S in concentrations less than 1 ppm. As a further precaution at the pilot plant site, personnel were furnished with individual Metronics H_2S detection tabs to be worn outside the garment. These tabs underwent a color change similar to that of lead acetate test strips upon exposure to H_2S. The extent of exposure could be estimated by comparing the detector color with a color key affixed to each tab.

Sulfur dioxide detection is less convenient than the qualitative H_2S methods described above; nevertheless, the ability to check rapidly for SO_2 is a critical safety requirement of this research. Sulfur dioxide may be detected conveniently by directing a stream of ammonia vapor toward the suspected source. (This can be done by use of a plastic wash bottle containing concentrated aqueous ammonia.) The presence of SO_2 is indicated by formation of a white cloud of ammonium sulfite.

For single analyses of various gases in large volume spaces, as in a laboratory or enclosed plant area, a Mine Safety Appliances Co. universal tester was used. This tester includes a hand-operated, piston-type pump and functions by aspirating a sample of the test atmosphere through a glass ampule containing a chemically treated substrate specific for the gas being analyzed. The concentration of the gas is estimated by comparing the extent of color development in the ampule with a key included in the test kit. This type of analyzer is capable of detecting low part-per-million concentrations of gases not easily measured otherwise under field conditions.

QUANTITATIVE ANALYSIS

Laboratory Tests

Gas Chromatography

The most useful analytical technique available during laboratory studies was gas chromatography. A single, isothermal chromatograph, equipped with a thermal conductivity detector and two analytical columns, was suitable for most analyses. Column selection was based upon the polarity of the gas. Because most gases tested during this program included both polar and nonpolar components, samples were usually injected onto two separate columns that differed greatly in polarity.

Samples were obtained in 50-cm^3 syringes and injected onto the columns by means of 500-μl gas sample loops. The reactivity of various components in typical samples made it necessary to perform analyses as soon after sampling as practicable; therefore, sample storage was not considered necessary or desirable.

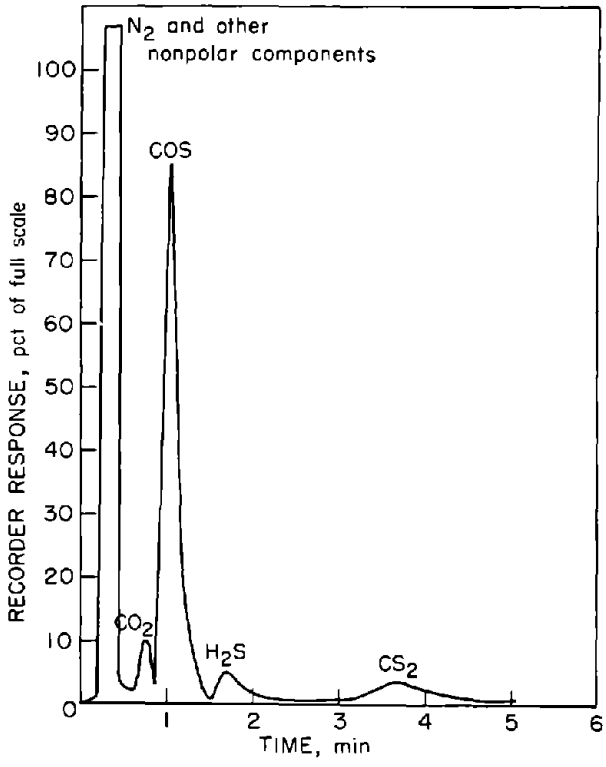

FIGURE 1. - Illustrative chromatogram—polar gas analysis.

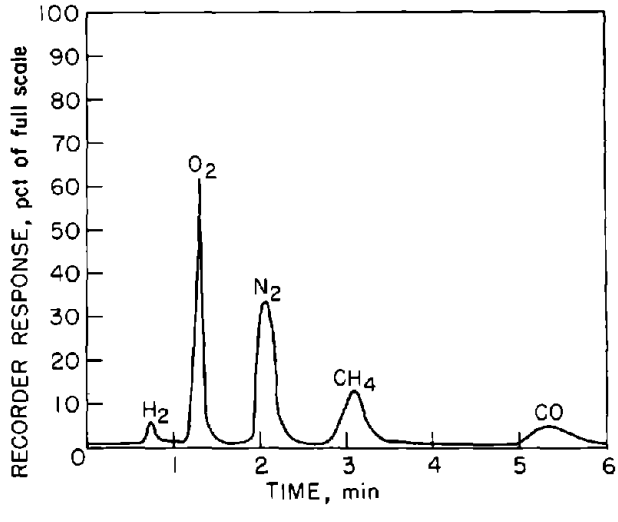

FIGURE 2. - Illustrative chromatogram—nonpolar gas analysis.

Chromatograph response was calibrated by use of purchased gas standards with compositions certified by the manufacturer to ±2 pct with respect to each component for concentrations greater than 50 ppm; for component concentrations below 50 ppm, certification accuracy was ±5 pct.[6] Such standards were verified as necessary by use of a Tutweiler gas buret (6). Chromatograms were recorded by use of conventional strip chart recorders and were quantified by peak integration. Most integrations were performed with Disc Instruments mechanical integrators; however, one chromatograph, procured for pilot plant experiments and used later in laboratory tests, was equipped with a Hewlett-Packard model 7123 recorder having an electronic integrator.

Polar Gases

Gases of moderate to high polarity include SO_2, H_2S, CO_2, COS, and CS_2. Mixtures containing these gases were analyzed by an adaptation of the method of Thornsberry (7). Figure 1 illustrates the analysis of a mixture of these gases. Sulfur dioxide, which was not detected in this sample, elutes after the CS_2 peak. The analytical column was a 1/4- by 18-inch stainless steel tube packed with commercial, acid-washed, 80- to 100-mesh silica gel. Oven and detector temperatures were 108° and 154° C, respectively. The filament current was 167 ma (milliamperes) and helium carrier flow was 55 cm^3/min.

Nonpolar gases

Nonpolar gases and those of only slight polarity include O_2, N_2, CO, H_2, and the hydrocarbons. Except for H_2 and the hydrocarbon gases, these were

[6] Standard gas mixtures purchased primarily for chromatograph calibration were also used for calibrating other instruments described herein.

analyzed routinely using a 1/4-inch by 6-foot stainless steel column packed with 100- to 120-mesh 5A molecular sieves (synthetic zeolite). Figure 2 shows the elution order and peak shapes obtained in a typical analysis of H_2S^- generator product. The oven and detector were at 108° C and 154° C, respectively. Filament current was 167 ma, and the helium carrier flow rate was 55 cm^3/min.

Hydrogen was analyzed by use of a 3/16-inch by 6-1/2-foot aluminum column packed with 42- to 60-mesh 5A molecular sieves. For this analysis, nitrogen carrier was used at a flow rate of 24 cm^3/min. The column was at room temperature, and the detector was at 70° C. Filament current was 60 ma. Nitrogen carrier provided greater sensitivity for hydrogen than can be attained with helium carrier.

Hydrocarbon gases were analyzed with a 1/2-inch by 3-foot stainless steel column packed with 80- to 100-mesh Porapak N adsorbent. Oven and detector temperatures were 50° C and 200° C, respectively. Filament current was 175 ma, and helium carrier flow was 25 cm^3/min. This analysis was required infrequently, mainly to verify the composition of the natural gas reductant used for H_2S generation.

Electrochemical Methods

Nitrogen Oxides

During studies of factors affecting oxidation in the citrate process, it became necessary to analyze for NO and NO_2. For these analyses, an EnviroMetrics Model NS-2000A electrochemical analyzer was used to rapidly measure nitrogen oxide concentrations between 50 and 1,000 ppm with estimated reliability of at least ±5 pct. This instrument is designed for analysis of both nitrogen oxides and SO_2, and, during the present investigations, it was used extensively for simultaneous analysis of these gases. Data for one gas at a time are displayed on a built-in meter that may be switched between two read positions to provide results for either of two different gases; alternatively, a two-pen strip chart recorder can be used to record both gas concentrations simultaneously and continuously. The EnviroMetrics analyzer can be made to operate over a broad range of concentrations by substituting an appropriate electronic component. The maximum sensitivity claimed by the manufacturer is 0.1 ppm for both SO_2 and NO or NO_2.

Continuous SO_2 Analysis

The continuous laboratory analysis of SO_2 was most frequently accomplished with Bureau-developed apparatus for automatically oxidizing the SO_2 to sulfate (SO_4^{2-}) and measuring the electrical conductivity of the resulting solution (1). Figure 3 is a schematic diagram of the apparatus. A 1-pct solution of H_2O_2, having a resistance of greater than 50,000 ohms and a pH value of 4.5, is fed with a metering pump at 6 ml/min onto the top of a 30-cm by 14-mm-diam glass column filled with 4-mm glass beads. The gas being analyzed is fed without dilution at 1 l/min into the bottom of the column by means of a tubing pump. Gas exiting the top of the column passes through a flowmeter. The

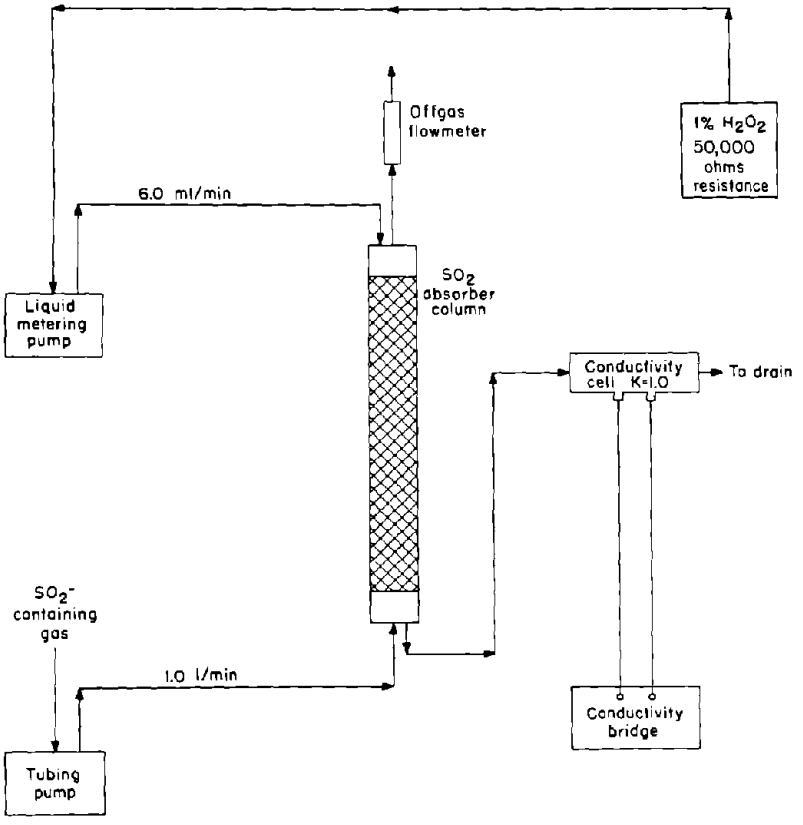

FIGURE 3. - Schematic diagram of conductivity apparatus for continuous SO_2 analysis.

solution leaving the bottom of the flooded column passes through a conductivity cell having a cell constant of 1.0. The resistance is measured with a conductivity bridge which has a range of 10 to 100,000 ohms. This method was found to be convenient and economical for long-term, continuous measurement of SO_2 at concentrations between 40 ppm and about 1 pct. A calibration curve of log cell resistance versus log SO_2 concentration is nearly linear over this range.

Infrared Spectroscopy

In most cases, satisfactory gas analyses were obtainable by the foregoing methods; however, during H_2S-generation experiments, it was necessary to screen product gas for minor amounts of possible side products, such as SO_2 and HCN in the presence of great excesses of major product. To measure the side products, infrared spectroscopy was used.

Infrared spectra were recorded with a Perkin-Elmer model 283, double-beam, infrared spectrophotometer. The unit is equipped with a filter-grating optical system covering the range between 4,000 and 200 wave numbers. Two 10-cm demountable gas cells with potassium bromide windows were used in the study. Samples containing water vapor were dried through anhydrous calcium sulfate prior to filling the absorption cell.

Reference spectra were obtained for standard gases to establish absorption peak assignments. Figure 4 shows peaks from the various components of a calibration mixture containing 10.1 pct CO_2, 10.9 pct CO, 5.5 pct CH_4, and 62.6 pct N_2. Although H_2 and N_2 are noninfrared active in the region between 4,000 and 200 wave numbers, the other gases are easily identified from their characteristic spectra.

The spectrum of H_2S, shown in figure 5, is weak but complex, and includes a series of absorption bands that overlap the SO_2 spectrum in the region between 1,400 and 1,100 wave numbers; however, even low concentrations of SO_2 may be detected in a gas sample containing H_2S if the same H_2S concentration is placed in the reference cell. Operating the spectrophotometer in the

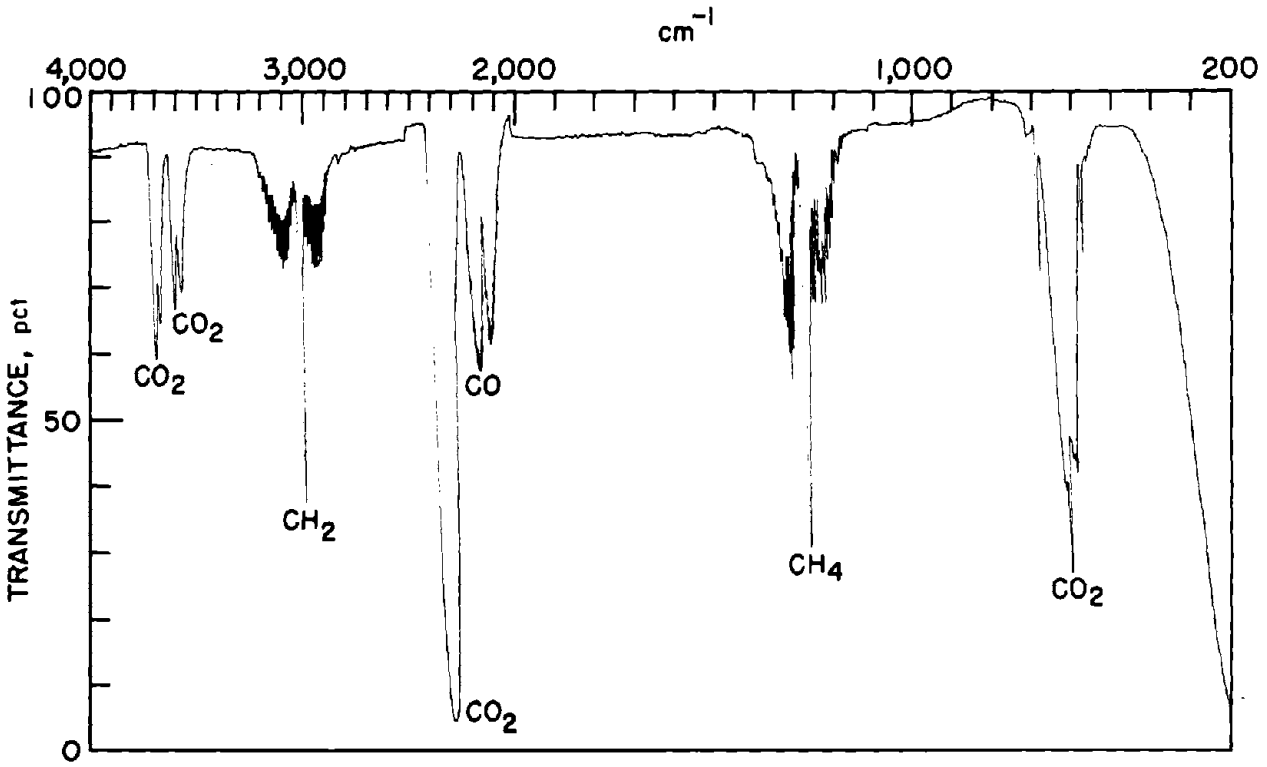

FIGURE 4. - Infrared spectrum of standard gas mixture.

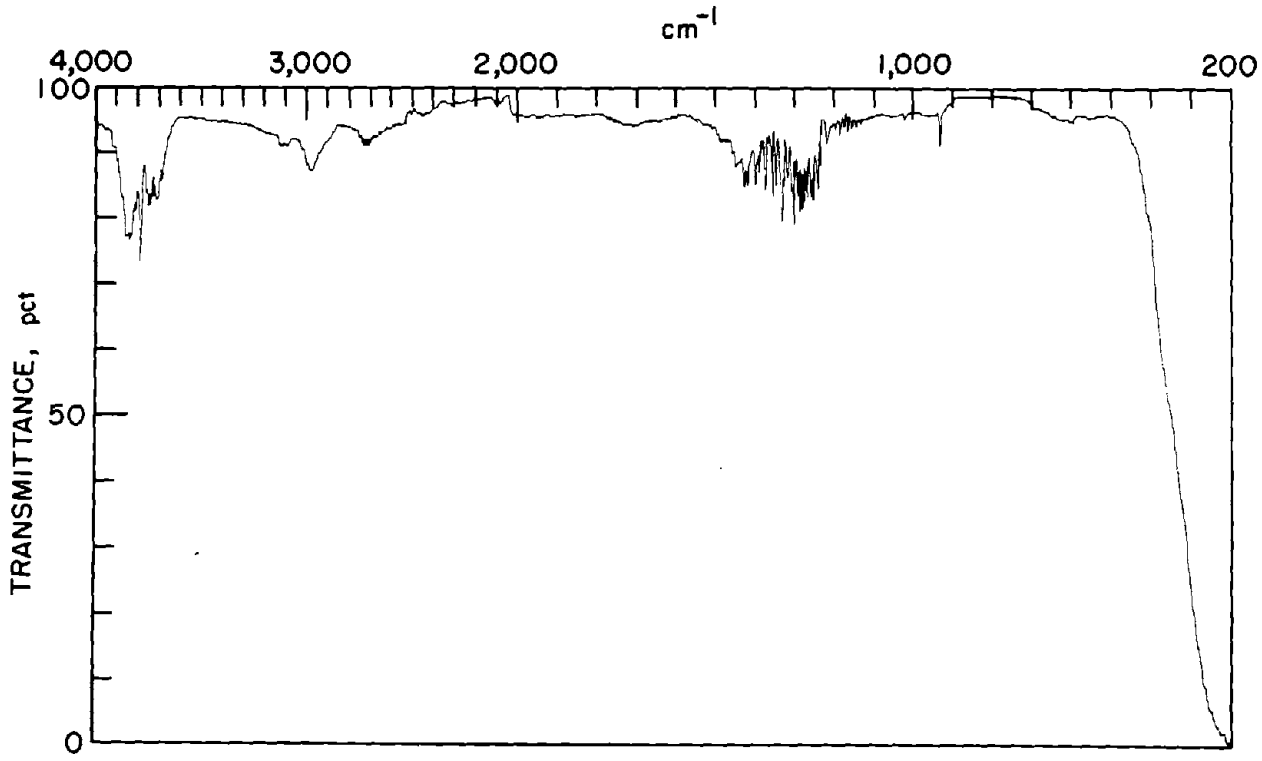

FIGURE 5. - Infrared spectrum of 100 pct H_2S.

double-beam mode electronically "subtracts" H_2S absorptions, enabling identification of absorptions attributable to SO_2.

Figure 6 shows the spectrum of SO_2 at a concentration of 0.44 pct in nitrogen. The sensitivity of this method for measuring SO_2 in a gas sample is demonstrated by figure 7, which shows absorption in the 1,350 wave number region by a standard sample containing only 0.0091 pct SO_2 in nitrogen. This partial spectrum was recorded by means of a tenfold absorption-scale expansion and 24-minute, full-scale recording interval, which greatly increased the instrument sensitivity. A concentration of 0.002 pct SO_2 could easily be detected by this technique.

Of the gases encountered in this study, only NO_2 and, to a lesser extent, methane (CH_4) interfere with analyzing low SO_2 concentrations by IR spectroscopy. Interferences could be overcome by use of a properly prepared reference cell to electronically subtract absorbance by the interfering component, but it would probably be advisable to use an alternate method such as the Enviro-Metrics or Meloy analyzer for gases containing significant concentrations of NO_2 or CH_4. Additional useful information is contained in the article by Pierson (3).

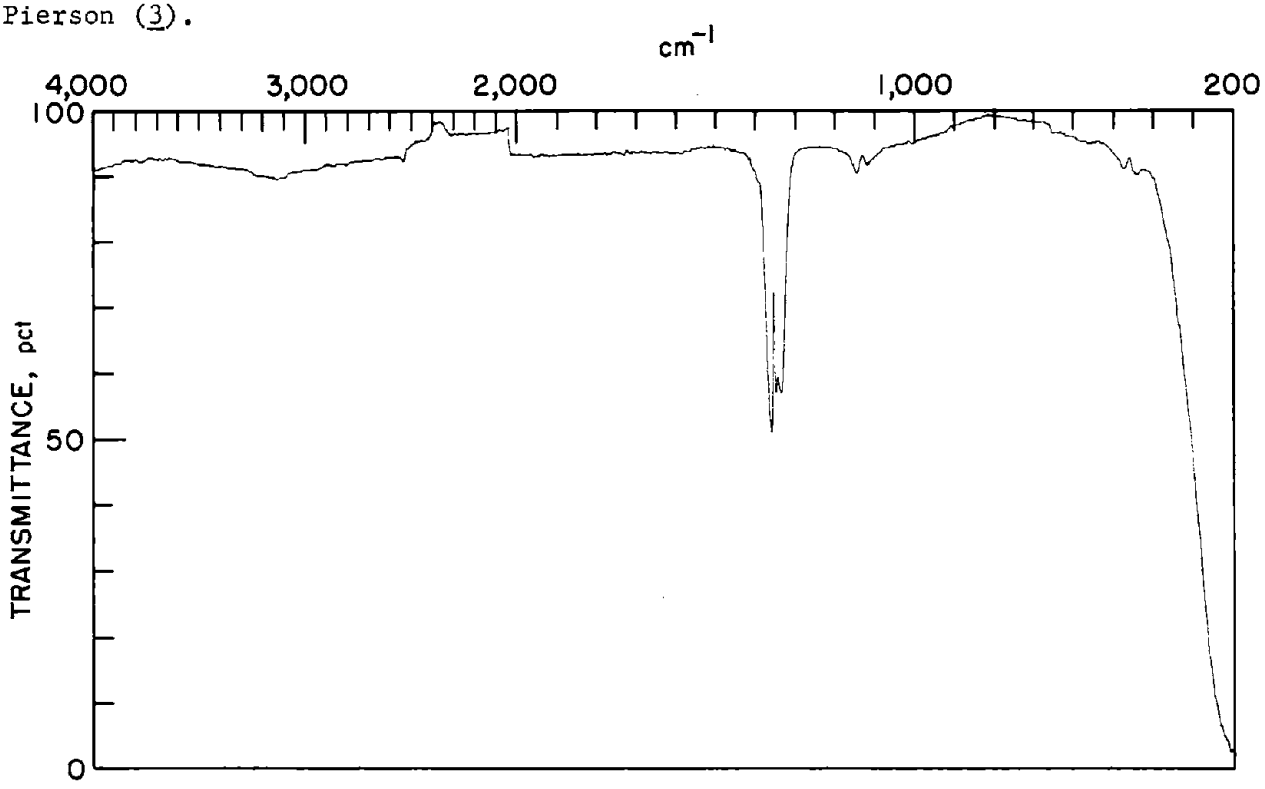

FIGURE 6. - Infrared spectrum of 0.44 pct SO_2 in nitrogen.

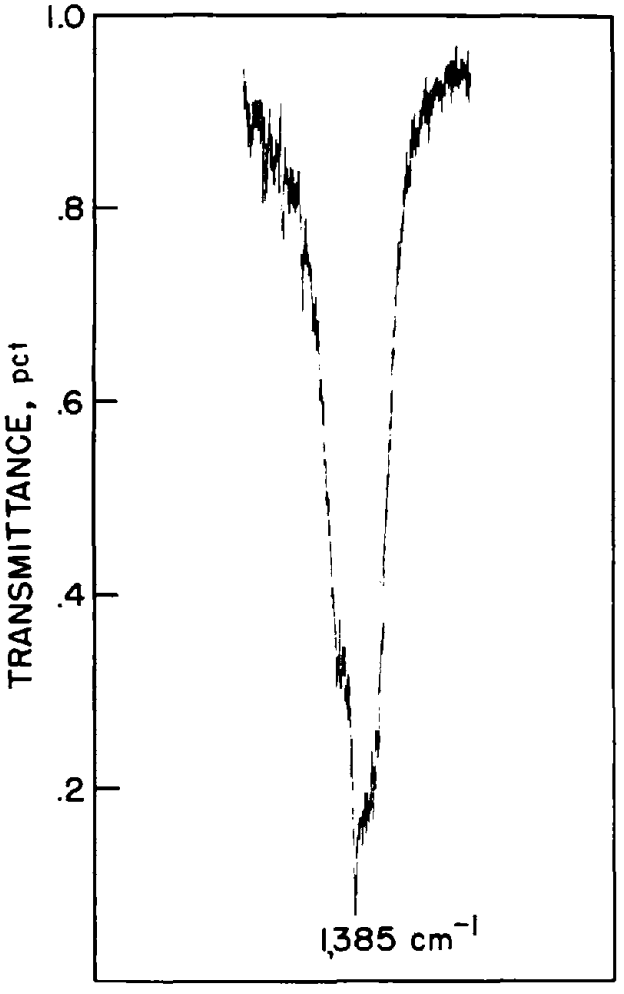

FIGURE 7. - Partial infrared spectrum of 0.0091 pct SO_2 in nitrogen.

In figure 8, the spectrum of COS is shown. This gas, which remains in the product as a result of incomplete reaction in the H_2S-generator, was present in most generator samples examined. Figure 9 is the spectrum of typical H_2S-generator product and shows the presence of both CO_2 and COS; however, SO_2, which absorbs strongly in the region between 1,400 and 1,050 wave numbers, was not detected in such samples.

It was feared that HCN might be formed in the H_2S generator. The spectrum of HCN gas is shown in figure 10. The distinctive absorptions in the 3,300 wave number region should make detection of this gas easy; none was found in any H_2S-generator product sample.

Computer Simulations

To facilitate evaluation of citrate process safety, a computer program for predicting product composition was used to simulate H_2S-generation experiments under widely varying conditions of temperature, pressure, and stoichiometry. This program was used to predict the existence of possible minor products that might not have been detected otherwise.

The composition of a complex mixture of gases at equilibrium can be predicted by the free energy minimization (FEM) method of White (8). In addition to predicting the abundance of trace components which may perturb the system or be hazardous to operators, the FEM method may be used to predict the effect of system changes upon various constituents--for example, the variance of COS concentration with excess steam or sulfur. The principal limits to its usefulness are the availability of thermodynamic data and the imagination of the program user.

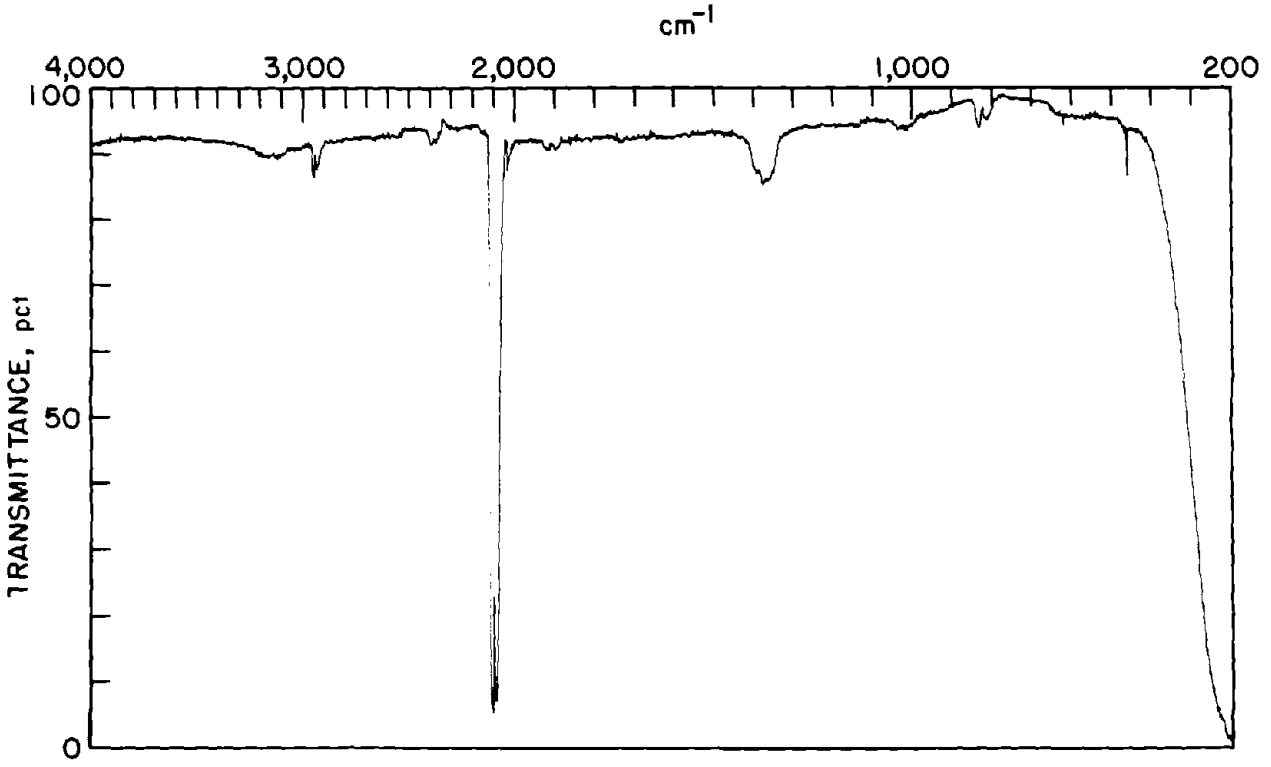

FIGURE 8. - Infrared spectrum of 0.95 pct COS in nitrogen.

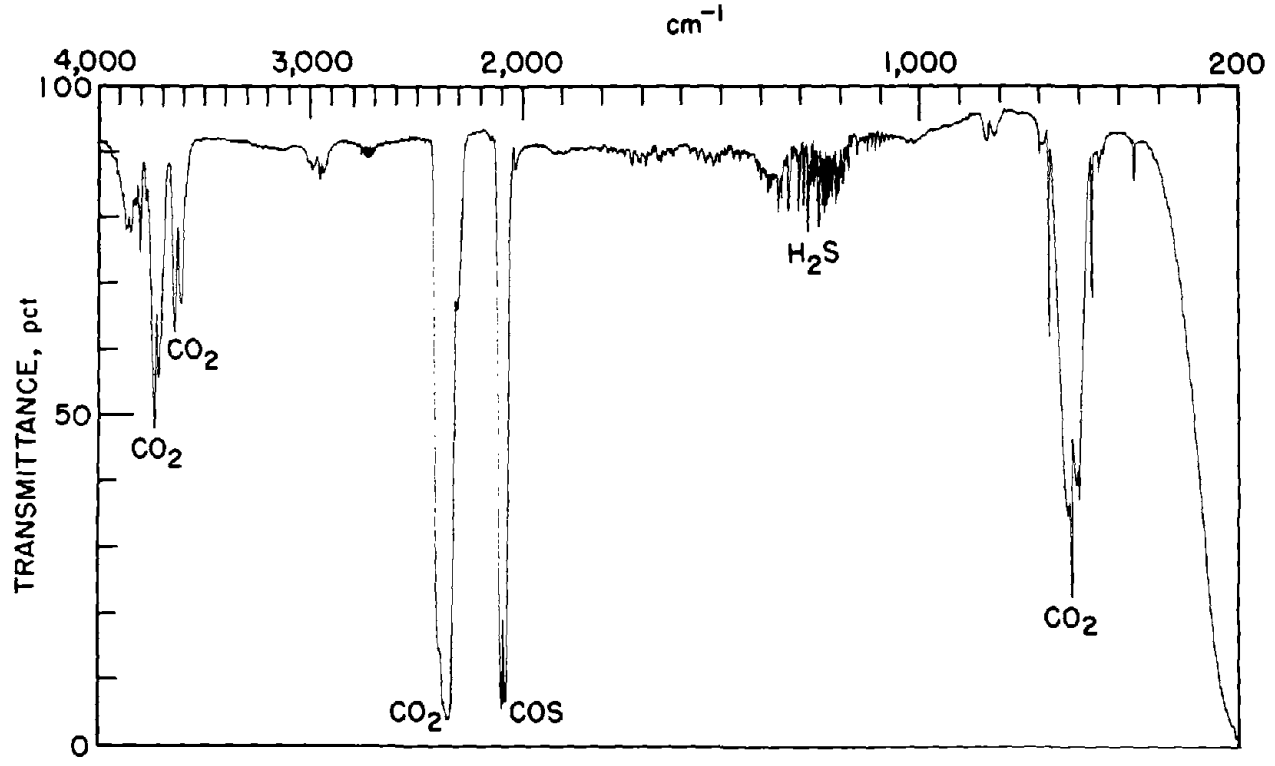

FIGURE 9. - Infrared spectrum of H_2S-generator product.

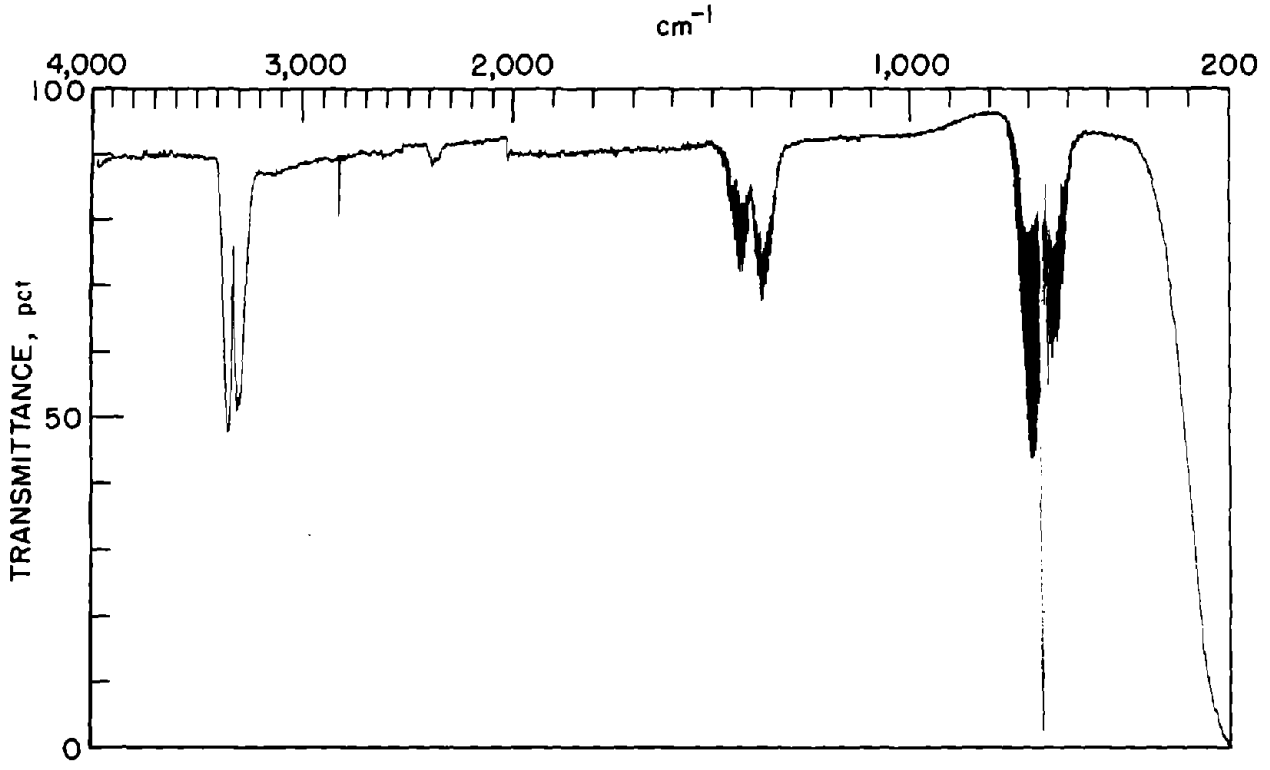

FIGURE 10. - Infrared spectrum of HCN.

The basic equation for system free energy, F(x), is:

$$F(x) = \sum_{i=1}^{n} x_i \left[\left(\frac{F^\circ}{RT} \right)_i + \ln P + \ln \frac{x_i}{\bar{x}} \right]$$

where n = total number of species present,

x_i = moles of the ith species,

$\frac{F^\circ}{RT}$ = standard molal Gibbs free energy function,

P = total pressure, atmospheres,

and $\bar{x} = \sum_{i=1}^{n} x_i$.

The value of F(x) is brought to a minimum by an iterative assignment of values to x_i that satisfy mass balance requirements until a preselected degree of accuracy is obtained, as described in footnote 6. This method was applied to H_2S-generation simulations for both the conditions prevailing at the Bunker Hill pilot plant and smaller scale tests at the Salt Lake City Metallurgy

Research Center. Table 1 compares typical product analyses with the corresponding computer-predicted composition. These data refer to H_2S produced by reducing elemental sulfur with natural gas in the presence of excess steam. Additional simulations were made that included a total of 54 different compounds as possible products. These included various aromatic and aliphatic hydrocarbons, sulfoxides, sulfones, thiols (mercaptans), sulfides, and such radicals as CH, NH, and SO. No unusual or previously undetected compound was predicted to be in the product gas by any of these simulations.

Table 1. - Comparison of analyzed composition with corresponding computer prediction for representative H_2S-generator-product samples

Sample description	Concentration, vol-pct									
	H_2S	CO_2	CO	CH_4	N_2	O_2	CS_2	COS	H_2	SO_2
Bunker Hill H_2S:										
Analyzed.....	76	18	0	3.5	1	-	0	1.3	-	-
Predicted.....	79	18	.1	0	.05	-	.1	2.8	0.06	0.09
Salt Lake City H_2S:										
Analyzed.....	79	21	0	.01	1.8	0.2	0	1.7	.8	-
Predicted.....	77	19	.5	0	1.0	0	.01	1.0	1.1	.3

Pilot Plant Tests

In general, gas analysis procedures used in the laboratory were adapted to the pilot plant tests; however, SO_2 analysis was a notable exception. Process control required continuous, automatic monitoring of the SO_2 concentration in both plant feed and offgas, at typical levels of 0.5 and 0.01 pct, respectively. For this application, a sulfur gas analyzer with Dyfusatron (by Meloy Laboratories, Inc.) was used. Sample streams comprising approximately one one-thousandth of total gas flow were withdrawn continuously from the bottom (feed gas) and top (offgas) of the absorber tower and fed into the analyzer. The corresponding SO_2 concentrations were automatically transmitted at alternating intervals to a remote strip chart recorder. The SO_2 analyzer unit is capable of analyzing SO_2 as low as 0.01 ppm; therefore, to accomodate pilot plant feed and offgas at 5,000 ppm and 100 ppm, respectively, the analyzer was coupled to a Dyfusatron unit that automatically diluted the SO_2 concentration to a level compatible with analyzer sensitivity. This equipment was capable of continuous SO_2 analysis at levels as low as 40 ppm with accuracy of ±5 pct. Regeneration reactor offgas was analyzed for H_2S by gas chromatography as described in the "Laboratory Tests" section.

RECOMMENDATIONS

The procedures described above proved adequate in providing the analytical support necessary during development of the citrate process from laboratory bench-scale tests to a pilot plant treating 1,000 std ft^3/min of lead smelter stack gas containing 0.5 pct SO_2. Some appropriate combination of these methods should satisfy the needs of workers using widely varying flue gas desulfurization techniques; however, two improvements in gas chromatographic capability would make many of these analyses both more rapid and more sensitive: (1) The chromatographs available during Bureau research were

equipped with thermal conductivity detectors. Much greater sensitivity is achievable, especially for sulfur-containing components, by use of flame-photometric detectors. Most manufacturers offer instruments having this type detector. (2) To permit adequate separation of the earlier-eluting components of gas mixtures, analyses were performed with oven temperatures of about 100° C. This relatively low temperature resulted in slow elution of some components such as CS_2, SO_2, and CO (see figs. 1-2), and caused these peaks to be poorly resolved. Use of a temperature-programmable chromatograph would permit the oven temperature to be increased systematically during each analysis. This would both shorten the time for elution of the last components, particularly SO_2, and improve peak symmetry. These two changes in GC procedure would yield improvements in efficiency and sensitivity which would amply justify the increased cost of more sophisticated instrumentation.

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15. Supplementary Notes

16. Abstract (Limit: 200 words): The citrate process for sulfur dioxide emission control was developed in pursuit of the Bureau of Mines goal of minimizing the adverse environmental impact of mineral-processing operations. This publication describes the gas analysis procedures used during development of the process. The research required the capability to analyze SO_2, H_2S, CO, CO_2, COS, volatile hydrocarbons, NO, NO_2, O_2, N_2, and H_2. The methods described include gas chromatography, electrochemical detection, infrared spectroscopy, and the use of a computer program to predict the product composition in complex reactions. Laboratory and pilot plant applications are discussed.

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