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CHEMISTRY OF FLUE GAS COMBINED NO<sub>x</sub> AND SO<sub>2</sub> SCRUBBER EMPLOYING FERROUS CYSTEINE ADDITIVES

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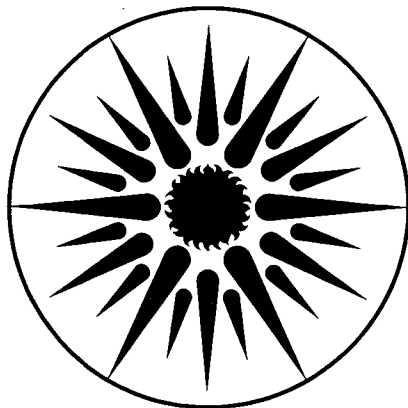
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CHEMISTRY OF A FLUE GAS COMBINED NO<sub>x</sub> AND SO<sub>2</sub>  
SCRUBBER EMPLOYING FERROUS CYSTEINE ADDITIVES

M.D. Tu and S.G. Chang

April 1986

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# Chemistry of a Flue Gas Combined NO<sub>x</sub> and SO<sub>2</sub> Scrubber Employing Ferrous Cysteine Additives

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## Abstract

Employment of ferrous cysteine additives creates different and simpler scrubber chemistry, compared to Japanese processes using ferrous chelates such as Fe<sup>2+</sup>(EDTA). Instead of being mainly converted to nitrous oxide, nitric oxide in flue gas can be concentrated and/or reduced to nitrogen gas, and production of dithionate ions and nitrogen-sulfur compounds in scrubbing systems can be suppressed or avoided. Fixation of nitric oxide can take place by rapid reaction with ferrous cysteine to form solid cystinatodinitrosyl iron (II) which can release NO upon heating. Cysteine can rapidly reduce ferric to ferrous ions while itself is oxidized to form cystine. The latter can be reduced back to cysteine by SO<sub>2</sub>.

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## I. Introduction

Japanese have developed a few flue gas simultaneous desulfurization and denitrification processes in the 1970s, and have shown that these wet processes are very efficient in  $\text{SO}_2$  and  $\text{NO}_x$  removal (more than 85% for  $\text{NO}_x$  and 95% for  $\text{SO}_2$ ). However, these wet processes have not reached the commercial stage yet because they are uncompetitive economically, according to cost evaluations.<sup>1,2</sup>

The most promising type of wet process developed so far is based on the addition of ferrous chelates in scrubbing liquors to enhance the absorption of NO by forming nitrosyl ferrous chelates in aqueous solutions. The nitrosyl ferrous chelates can then react<sup>1,3</sup> with dissolved  $\text{SO}_2$  and  $\text{O}_2$  to produce  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , dithionate, sulfate and various N-S compounds<sup>4,6</sup> using the type of chelates patented by the Japanese such as EDTA and NTA, while some ferrous chelates are oxidized by residual  $\text{O}_2$  in flue gas and by intermediates produced in the system to ferric chelates, which are inactive. Therefore, this type of process requires regeneration of scrubbing liquors by removing dithionate, sulfate, and N-S compounds from the solutions and reduction of ferric chelates back to ferrous chelates.

The regeneration of scrubbing liquors and ferrous chelates associated with Japanese's processes<sup>2</sup> are very costly. For example, in the Asahi process, scrubbing liquors are pumped to an evaporators in the regeneration system. The concentrated solution from the evaporators is then pumped to a cooling crystallizer where hydrated sodium dithionate and sulfate crystals are produced under vacuum. These crystals are separated from the mother liquor in a screw decanter and sent to a dryer operating at 250 °F-300 °F in which the hydrated crystals are converted to anhydrous sodium salts. Most of the mother liquors from the decanter is recycled to the reducing tank and a smaller stream is passed through a N-S compounds treatment section. The N-S compounds are converted to relatively insoluble potassium salts by reaction with potassium sulfate. The potassium salts of N-S compounds are separated in a screw decanter and sent to a thermal cracker for the decomposition at about 930 °F.

The high capital investment cost of the Asahi process is due to the necessity for large absorbers, evaporators, crystallizers, dryers, rotary kiln crackers and screw decanter separators. The major operating and maintenance costs are electricity, fuel oil, steam and chemicals such as soda ash, EDTA and limestone.

The requirement for consumption of large amount of utilities is associated with the operation principle and design of the Asahi process.

We have recently developed new additives for combined removal of  $\text{SO}_2$  and  $\text{NO}_x$  from flue gas.<sup>7,8</sup> The new additives include ferrous cysteine, alkalis, and borate. Employment of these new additives creates different and simpler scrubber chemistry compared to Japanese processes using ferrous chelates such as  $\text{Fe}^{2+}$ (EDTA). The production of dithionate and nitrogen-sulfur compounds can be suppressed or avoided by using these new additives. Ferric ions formed can be reduced by cysteine back to ferrous ions. This paper addresses the chemistry involving ferrous cysteine, NO,  $\text{SO}_2$ , and  $\text{O}_2$  that applies to a wet as well as spray drying flue gas clean up systems.

## II. Experimental Section

The reaction of ferrous cysteine with NO can behave differently depending on the molar ratio of cysteine to ferrous ion,  $n_{\text{cysteine}}/n_{\text{Fe}^{2+}}$ , and the pH of the solutions. We have performed experiments to determine the absorption capacity of NO in aqueous solutions containing ferrous cysteine complexes at various  $n_{\text{cysteine}}/n_{\text{Fe}^{2+}}$ , pHs and 55 °C using a bench-scale gas scrubber. Also, we have characterized the precipitates produced from reactions by means of an infrared spectroscopy and elemental analysis, and gaseous products by a mass spectrometry. Oxygen in flue gas can oxidize cysteine to cystine. This oxidation is catalyzed by ferrous ions. The effect of oxygen to the absorption of NO in ferrous cysteine solutions was also studied with the gas scrubber.  $\text{SO}_2$  in flue gas can reduce cysteine to cystine. The reaction of  $\text{SO}_2$  with cystine in solutions was characterized by laser Raman spectroscopy.

A general experimental procedure is outlined below for the case where  $n_{\text{cysteine}}/n_{\text{Fe}^{2+}}$  in the reaction mixture is 4 and the reaction temperature is 55 °C. In 200 ml distilled water were dissolved 6.866 gm ( $9 \times 10^{-2}$  M)  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  (Baker reagent) as buffer and 1.404 gm ( $4 \times 10^{-2}$  M) cysteine.HCl.H<sub>2</sub>O (Baker reagent). The pH of the solution was adjusted to the desired value by addition of NaOH or  $\text{H}_2\text{SO}_4$ . The solution was transferred to a reaction column (50 mm ID x 210 mm; pyrex) and then purged with  $\text{N}_2$  to remove  $\text{O}_2$  from the system. 0.784 gm ( $1 \times 10^{-2}$  M)  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (Mallinckrodt reagent) was

then added and the solution was again purged with  $N_2$ . The NO obtained from Matheson Co. was a mixture of 2.55% NO in  $N_2$  with  $NO_2$  impurity of less than 255 ppm; this NO was further diluted by adding  $N_2$  to between 650 and 1,000 ppm. The experiments were carried out by bubbling a mixture of NO and  $N_2$  of known NO concentration through a NaOH solution to absorb  $NO_2$  impurity in gas. This  $NO_2$ -free mixture of NO and  $N_2$  gas was then bubbled through the ferrous cysteine solution, and the NO concentration in the outlet gas was measured with a Thermoelectron Model 14A chemiluminescent  $NO_x$  analyzer. The gas flow rates were 630-800 mL/min. NO absorption was carried out until the NO concentration in the outlet gas became equal to that in the inlet gas, i.e., until saturation was reached. The resulting solutions were filtered in the absence of oxygen and the precipitates collected were dried in a vacuum desiccator. The precipitates were analyzed by infrared spectroscopy and elemental analysis.

Gaseous products were obtained when the reactions of NO with ferrous cysteine were carried out in a batch system at 25 °C using a vacuum line setup. 50 ml distilled water was placed in a 100 ml round bottom flask and 0.702 gm ( $8 \times 10^{-2}$  M) cysteine and 3.433 gm (0.18 M)  $Na_2B_4O_7 \cdot 10H_2O$  (as buffer) were added. The pH of the solution was adjusted to the desired value by addition of NaOH or  $H_2SO_4$ . The flask containing the reaction mixture was evacuated and then filled with argon gas. 0.392 gm ( $2 \times 10^{-2}$  M)  $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$  was added and the solution was again degassed. Pure NO (triple-distilled) was then expanded into the round bottom flask to about 760 mm Hg. The solution was stirred until the pressure over solutions was stable, and gas sample above the solution was allowed to expand into a previously evacuated flask for mass spectral analysis. The solution was then filtered, and the solid precipitates collected were dried and subjected to infrared studies and elemental analysis.

### III. Results and Discussions

Figure 1 shows the effect of pH on the absorption of NO when the reaction temperature is 55 °C and  $n_{\text{cysteine}}/n_{Fe^{2+}}$  is 4. The amount of NO absorbed per mole of  $Fe^{2+}$ ,  $n_{NO}/n_{Fe^{2+}}$ , and per mole of cysteine,  $n_{NO}/n_{\text{cysteine}}$ , increases from 0.5 to 2.7 and 0.12 to 0.70 respectively, as the pH of the solution increases from 6 to 8.  $n_{NO}/n_{Fe^{2+}}$  and  $n_{NO}/n_{\text{cysteine}}$  remain unchanged between pH 8 and 10. The effects of  $n_{\text{cysteine}}/n_{Fe^{2+}}$

on  $n_{\text{NO}}/n_{\text{Fe}^{2+}}$  and  $n_{\text{NO}}/n_{\text{cysteine}}$  at pH 7 and 8, and 55 °C are shown in Figure 2.  $n_{\text{NO}}/n_{\text{cysteine}}$  decreases steadily from 0.57 to 0.24 as  $n_{\text{cysteine}}/n_{\text{Fe}^{2+}}$  increases from 2 to 6 at pH 7. When pH is at 8,  $n_{\text{NO}}/n_{\text{cysteine}}$  increases from 0.39 to 0.7 as  $n_{\text{cysteine}}/n_{\text{Fe}^{2+}}$  increases from 2 to 4 and then gradually decreases to 0.64 at  $n_{\text{cysteine}}/n_{\text{Fe}^{2+}}$  of 6. This same behavior was observed for  $n_{\text{NO}}/n_{\text{Fe}^{2+}}$  in solutions at pH 7.  $n_{\text{NO}}/n_{\text{Fe}^{2+}}$  reaches the maximum value of 1.5 at  $n_{\text{cysteine}}/n_{\text{Fe}^{2+}}$  of 4 and decreases slightly with increasing  $n_{\text{cysteine}}/n_{\text{Fe}^{2+}}$  ratio. However, at pH 8,  $n_{\text{NO}}/n_{\text{Fe}^{2+}}$  increases monotonously from 0.78 to 3.82 as  $n_{\text{cysteine}}/n_{\text{Fe}^{2+}}$  increases from 2 to 6.

Varying the pH of the solution and the ratio of cysteine to  $\text{Fe}^{2+}$  not only affects the amount of NO absorbed but also changes the nature of the reaction products. Figure 3 shows the IR spectra of the precipitates obtained from the reaction of  $\text{Fe}^{2+} + 4$  cysteine with NO at 55 °C and different pH's. Also shown in Figure 3 are the IR spectra of solid cysteine and cystine for comparison. It is obvious from these IR results that the nature of the solid is very different when the pH of solutions is changed from 7 to 10. The IR spectrum of precipitates at pH 7 shows several bands at 350(sh), 515(m), 920(w), 990(w), 1140(sh), 1255(m), 1265(m), 1310(m), 1430(m), and 1775(s)  $\text{cm}^{-1}$ , in addition to all the bands of cystine. The band at 1775  $\text{cm}^{-1}$  can be attributed to the M-NO stretching  $\nu_{\text{M-NO}}$ . The relative intensity of this band decreases for solid precipitates obtained at pH 7.5, where the only other bands observed are those of cystine. The IR spectrum of solids at pH 8 shows different features than those at pH 7 and 7.5. The 1775  $\text{cm}^{-1}$   $\nu_{\text{M-NO}}$  band disappears, neither does those bands due to cystine as observed in solids obtained at pH 7 and 7.5. However, the absence of the cystine bending bands  $\delta_s\text{-NH}_3^+$  (1490  $\text{cm}^{-1}$ ),  $\delta_{\text{as}}\text{-NH}_3^+$  (1580 and 1620  $\text{cm}^{-1}$ ), and the stretching band  $\nu\text{-NH}_3^+$  (3030  $\text{cm}^{-1}$ ); and the presence of  $\nu_s\text{-NH}_2$  (3280  $\text{cm}^{-1}$ ),  $\nu_{\text{as}}\text{-NH}_2$  (3350 and 3370  $\text{cm}^{-1}$ ) indicate the bonding of the cystine amino group to the ferrous ion. The IR spectrum of solids at pH 10 resembles that of  $\text{Fe}(\text{OH})_2$  and/or  $\text{Fe}(\text{OH})_3$ . The complete assignments of IR bands are in progress. The IR results are in good agreement with results of elemental analysis. Table 1 shows the  $n_{\text{NO}}/n_{\text{Fe}^{2+}}$  and  $n_{\text{cysteine}}/n_{\text{Fe}^{2+}}$ , obtained from elemental analysis, in the precipitates of reactions at pH 7 and 8 and 55 °C. The solids at pH 7 contain two moles of NO per each mole of  $\text{Fe}^{2+}$  found (Table 2), whereas, the solids at pH 8 does not contain NO at all. The solids obtained from reactions at pH 10 and 55 °C contain only iron, but neither cysteine nor NO.

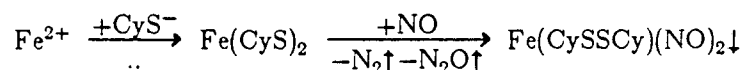


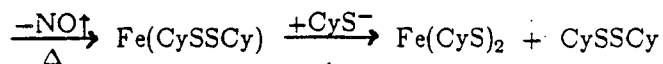
The influence of  $n_{\text{cysteine}}/n_{\text{Fe}^{2+}}$  on the nature of precipitates produced were studied. Figure 4 is the IR spectra of solids obtained at pH 7 and 55 °C. A strong band at 1775  $\text{cm}^{-1}$  was observed for all ratio of  $n_{\text{cysteine}}/n_{\text{Fe}^{2+}}$ . Additional bands at 515, 990, 1255, 1265, 1310, and 1430  $\text{cm}^{-1}$  appear for solids obtained when the ratio of  $n_{\text{cysteine}}/n_{\text{Fe}^{2+}}$  are more than 3. Figure 5 shows IR spectra of the precipitates collected from the reaction at pH 8 and 55 °C. There is no NO complex in the reaction products as evident from the absence of a band at 1775  $\text{cm}^{-1}$ . Notice the increase in the intensity of the bands at 550, 849, 1125, 1300, 1340  $\text{cm}^{-1}$ , as the  $n_{\text{cysteine}}/n_{\text{Fe}^{2+}}$  increases from 2 to 6. Additional bands at 775 and 1470  $\text{cm}^{-1}$  were observed for solids obtained when the ratio of  $n_{\text{cysteine}}/n_{\text{Fe}^{2+}}$  were 4, 5 and 6; and two more bands at 455 and 870  $\text{cm}^{-1}$  when the ratio is 5 and 6.

When the solid sample containing M-NO was subjected to heating ( $\sim 155$  °C) or vacuum ( $\leq 10^{-2}$  torr), NO would be released. Figure 6 shows the IR spectra of solids after heating at 155 °C for 2 and 7 hours. Part of the NO was released after heating the solid sample for 2 hrs, and all the NO had disappeared after heating for 7 hrs. Analysis of the gaseous species evolved after heating showed mostly NO with a trace of  $\text{N}_2\text{O}$ . This again confirms that absorbed NO is present in the solid precipitates.

The analyses of gaseous products, from the reaction of ferrous cysteine with NO, by mass spectrometry indicate that at pH 10, all the NO absorbed is reduced by the ferrous cysteine in solutions to yield a mixture of  $\text{N}_2$  (78.5%) and  $\text{N}_2\text{O}$  (21.5%). At pH 8, 46.5% of the absorbed NO is converted to a mixture of  $\text{N}_2$  (54.0%) and  $\text{N}_2\text{O}$  (46.0%), while the rest remained in the solutions (none in precipitates as can be seen in Table 1). At pH 7, 45.7% of the absorbed NO is reduced to a mixture of  $\text{N}_2$  (46.7%) and  $\text{N}_2\text{O}$  (50.3%). The rest of the absorbed NO presumably ends up in the precipitates (Figure 4 and Tables 1 and 2) and possibly some remaining in liquid solutions.

The reactions of NO with ferrous cysteine in solutions behave differently depending on the concentration of reactants and pH of the solutions. The reactions involved have not been well characterized, however, the following reaction sequences appear to take place.

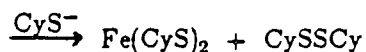
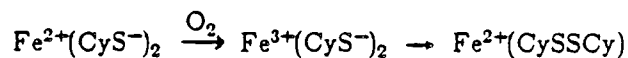




Where CyS and CySSCy are cysteine and cystine respectively.

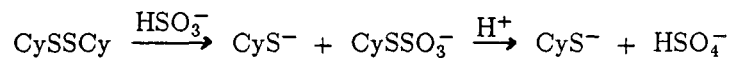
Oxygen, in the amount of about 5% in flue gas, can dissolve in ferrous cysteine solutions and oxidize the ferrous ion to ferric ion and thus decrease NO absorption efficiency. An experiment was carried out by bubbling a mixture of gases containing 800 ppm NO and 5% O<sub>2</sub> with the remaining N<sub>2</sub> into a 10<sup>-2</sup> M ferrous cysteine solutions (molar ratio of cysteine to ferrous ion was 1). The result shows a substantial 92.8% reduction in NO absorption, compared to the case where there was no oxygen in flue gas (Table 3). A separate run was conducted for solutions containing Fe<sup>2+</sup>(EDTA) under similar conditions to those used for Fe<sup>2+</sup>(cysteine). The results indicated a 90% reduction in NO absorption with the presence of 5% O<sub>2</sub>. The absorption capacity of NO in Fe<sup>2+</sup>(cysteine) solutions is almost twice as much as that in Fe<sup>2+</sup>(EDTA) solutions without the presence of O<sub>2</sub> and about 30% more efficient with 5% of O<sub>2</sub> under experimental conditions employed (Table 3).

Once ferrous ion is oxidized to ferric ion by O<sub>2</sub>, cysteine can rapidly reduce ferric back to ferrous ion while itself is oxidized to cystine. Reactions of O<sub>2</sub> with ferrous cysteine in solutions can be represented by



Sulfite and bisulfite ions do not appear to react with coordinated NO in ferrous nitrosyl cysteine complexes, however, they do react with cystine to form cysteine and thiocysteine as shown in Figure 7. The Raman shifts at 934, 967, and 1023/1055 cm<sup>-1</sup> correspond to ClO<sub>4</sub><sup>-</sup>, SO<sub>3</sub><sup>2-</sup>, and HSO<sub>3</sub><sup>-</sup> respectively, where ClO<sub>4</sub><sup>-</sup> was used as a reference compound. A new Raman peak at 1027 cm<sup>-1</sup> appears after mixing the SO<sub>3</sub><sup>2-</sup>/HSO<sub>3</sub><sup>-</sup> with cystine/ClO<sub>4</sub><sup>-</sup> solutions. The 1027 cm<sup>-1</sup> peak corresponds to thiocysteine. The Raman shifts for cysteine and cystine are too weak to be detected at the concentrations employed. The equilibrium constants of the reactions have been determined at various pHs.<sup>4</sup>

Thiocysteine can undergo hydrolysis to produce cysteine and sulfate. The hydrolysis rate is acid catalyzed and is very slow unless at very low pH conditions. Reactions of  $\text{SO}_2$  with cystine in solutions can be shown as follows:



#### IV. Conclusion

The cysteine can bind to ferrous ion to form ferrous cysteine which can efficiently bind and react with NO to form cystinatodinitrosyl iron(II)  $\text{Fe}(\text{CySSCy})(\text{NO})_2$ . When ferrous ion is oxidized to ferric ion by residual oxygen in flue gas, cysteine can reduce ferric back to ferrous ion very quickly, while, cysteine is reduced to cystine, which is a dimer of cysteine. Both cystine and cystinatodinitrosyl iron(II) are not very soluble in neutral aqueous solutions, and will precipitate. Cystinatodinitrosyl iron(II) can undergo thermodecomposition at relatively low temperature ( $T \sim 150^\circ\text{C}$ ) to produce ferrous cysteine and release NO. The concentrated NO gas can be recycled into the boiler or used for  $\text{HNO}_3$  manufacturing. The ferrous salts can be recycled. The cystine can dissolve in basic solutions and be reduced to cysteine for recycle by either chemical or electrochemical reduction methods, which are commercial available techniques. Also, the cystine can be reduced by absorbed  $\text{SO}_2$  (sulfite/bisulfite) to produce cysteine and cysteinesulfonate which undergoes acid catalyzed hydrolysis to form cysteine and sulfate.

In the Japanese processes, dithionate ion is produced as a result of the reduction of ferric ion by bisulfite, and N-S compounds are produced as a result of reaction between  $\text{Fe}^{2+}(\text{EDTA})\text{NO}$  and bisulfite/sulfite. In processes using ferrous cysteine additives, ferric ion can be reduced by cysteine rapidly, therefore, minimizing the possibility for ferric ion to interact with bisulfite, the dithionate formation can be minimized or eliminated as a result. Also, the coordinated NO in cystinatodinitrosyl iron(II) does not appear to react with dissolved  $\text{SO}_2$  to produce N-S compounds.

Spray drying systems have been demonstrated to be more cost-effective than wet systems for control of  $\text{SO}_2$  emissions from power plants. The addition of metal chelates to the alkali spray slurries for simultaneous control of  $\text{SO}_2$  and  $\text{NO}_x$  could be very effective. The  $\text{Fe}^{2+}(\text{EDTA})$  and  $\text{Fe}^{2+}(\text{NTA})$  type

metal chelates are not suitable for use in spray drying systems, however, because the metal chelates suitable for employment in spray drying systems must be able to absorb or react with NO irreversibly under the scrubbing conditions. As the droplet passes through the flue gas, it will heat up. This has the effect of reducing the liquid volume through evaporation and changing the kinetics due to the temperature dependence of the rate constants and equilibrium constants. If the droplet loses all its water by evaporation, the NO attached to  $\text{Fe}^{2+}(\text{EDTA})$  or  $\text{Fe}^{2+}(\text{NTA})$  type ferrous chelates will dissociate and return to the gas phase. From the kinetic information, one can calculate that only a small fraction of absorbed NO will react with dissolved  $\text{SO}_2$  during less than 10 sec residence time of the droplet in spray drying chamber.

Unlike  $\text{Fe}^{2+}(\text{EDTA})$  and  $\text{Fe}^{2+}(\text{NTA})$ , absorption of NO to ferrous cysteine is not reversible and undergoes a chemical change to produce cystinatodinitrosyl iron(II). This product is stable in solid form and would not release NO even at NO-free atmosphere unless heat or evacuation is applied. The reaction rate of NO with ferrous cysteine has not been measured, indications from absorption experiments are that it is probably as fast as that of NO with  $\text{Fe}^{2+}(\text{EDTA})$ , i.e.,  $\geq 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ . Therefore ferrous cysteine appears to possess the right property for use with alkali such as lime/limestone or trona/NaOH in spray drying systems for combined removal of  $\text{NO}_x$  and  $\text{SO}_2$  from flue gas. A cost-effective method for regeneration of cysteine from cystine is also available.<sup>9</sup>

### Acknowledgement

We appreciate the support and encouragement of Michael Perlsweig, Joseph Strakey, and John Williams.

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$n_{\text{cysteine}}/n_{\text{Fe}^{2+}}$		2	3	4	5	6
pH 7	$\frac{n_{\text{NO}}}{n_{\text{Fe}^{2+}}}$	1.95	1.9	2.2	2.1	1.92
	$\frac{n_{\text{cysteine}}}{n_{\text{Fe}^{2+}}}$	3.0	2.0	2.0	4.3	2.0
pH 8	$\frac{n_{\text{NO}}}{n_{\text{Fe}^{2+}}}$	0	0	0	0	0
	$\frac{n_{\text{cysteine}}}{n_{\text{Fe}^{2+}}}$	1.73	2.07	2.14	2.83	3.42

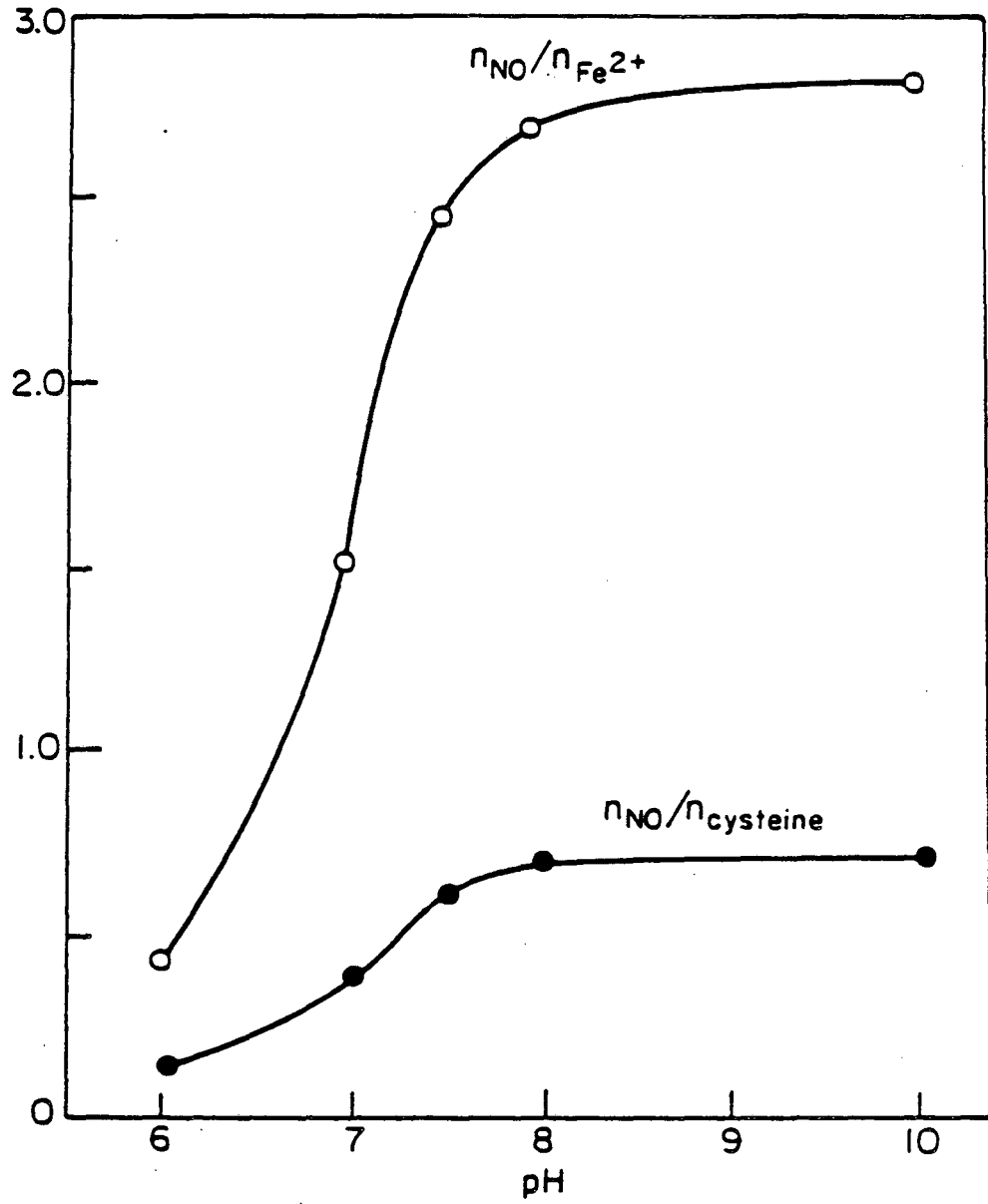
$n_{\text{cysteine}}/n_{\text{Fe}^{2+}}$	C (%)	H (%)	N (%)	S (%)	Fe (%)	Empirical Formula
2	20.27	3.80	11.90	16.69	9.59	$\text{Fe}(\text{C}_3\text{H}_7\text{NS})_3(\text{NO})_2$
3	19.66	3.40	14.85	17.73	14.70	$\text{Fe}(\text{C}_3\text{H}_6\text{NS})_2(\text{NO})_2$
4	20.88	3.60	14.83	17.82	13.10	$\text{Fe}(\text{C}_3\text{H}_6\text{NS})_2(\text{NO})_2$
5	24.26	4.18	13.48	20.56	8.65	$\text{Fe}(\text{C}_3\text{H}_7\text{NS})_4(\text{NO})_2$
6	19.67	3.58	14.15	17.10	14.12	$\text{Fe}(\text{C}_2\text{H}_7\text{NS})_2(\text{NO})_2$

<p style="text-align: center;"><b>Table 3</b></p> <p style="text-align: center;"><b>Comparison of NO absorption Capacity in Aqueous Solutions Containing Fe<sup>2+</sup> (cysteine) and Fe<sup>2+</sup> (EDTA)</b></p> <p style="text-align: center;">(Fe<sup>2+</sup> = cysteine = EDTA = 10<sup>-2</sup> M, P<sub>NO</sub> = 800 ppm, pH = 7 and at 55 °C)</p>		
Metal Complexes	O <sub>2</sub>	NO absorbed (M)
Fe <sup>2+</sup> (cysteine)	0	9.0 x 10 <sup>-3</sup>
	5%	6.5 x 10 <sup>-4</sup>
Fe <sup>2+</sup> (EDTA)	0	5.0 x 10 <sup>-3</sup>
	5%	5.1 x 10 <sup>-4</sup>



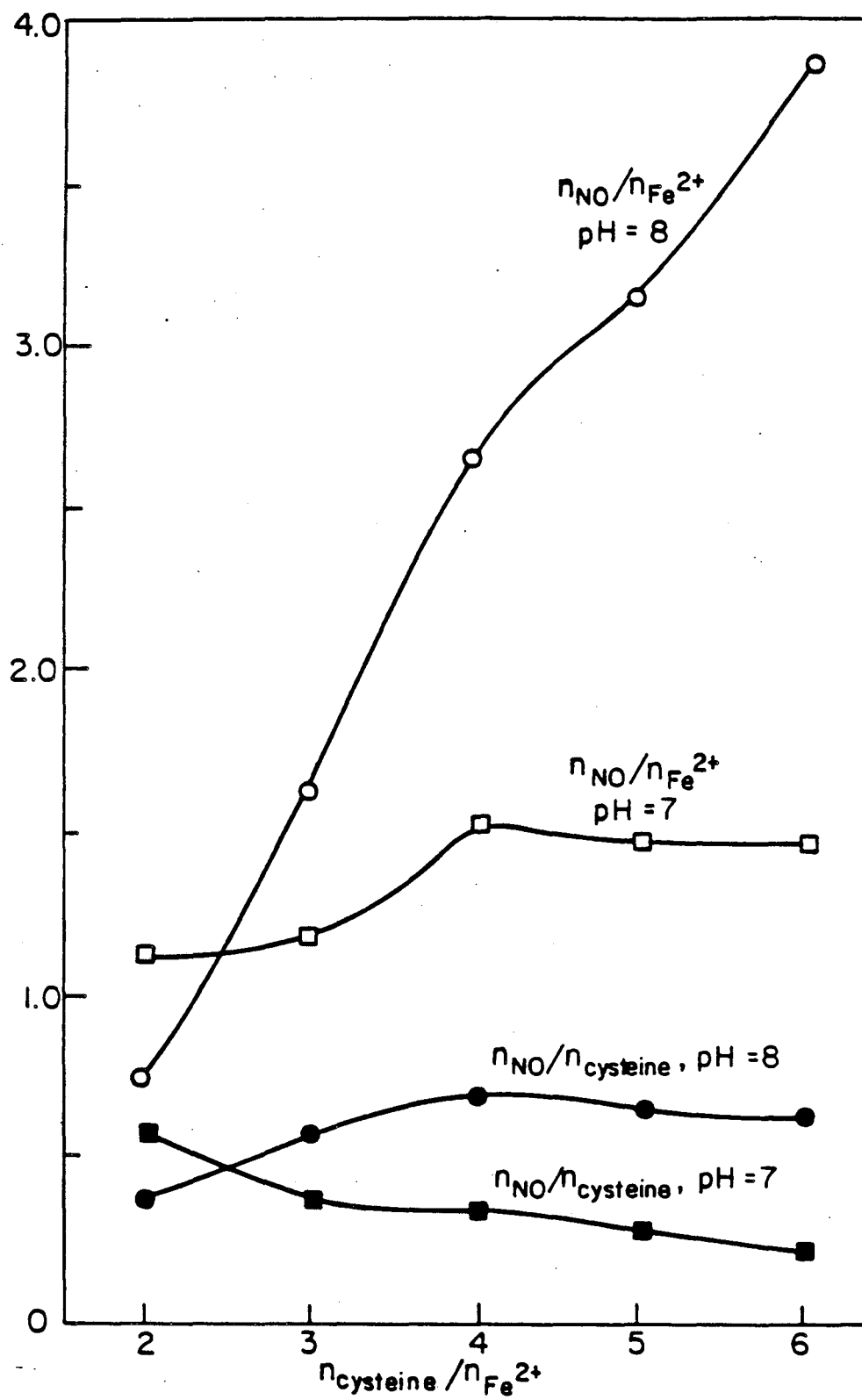
## Figure Captions

- Figure 1.** The effect of pH on the absorption of NO in aqueous solutions containing ferrous cysteine, with molar ratio of cysteine to ferrous ion of 4 and at 55 °C.
- Figure 2.** The effect of molar ratio of cysteine to ferrous ion on the absorption of NO in solutions at pH 7 and 8, and 55 °C.
- Figure 3.** Infrared spectra of cysteine, cystine, and solid products of reaction  $\text{Fe}^{2+} + 4 \text{cysteine} + \text{NO}$  at different pHs and 55 °C.
- Figure 4.** Infrared spectra of solid products from reactions of NO with ferrous cysteine, at various molar ratios of cysteine to ferrous ion and at pH 7 and 55 °C.
- Figure 5.** Infrared spectra of solid products from reaction of NO with ferrous cysteine, at various molar ratios of cysteine to ferrous ion and at pH 8 and 55 °C.
- Figure 6.** Infrared spectra showing the thermal stability (at 155 °C) of solid products obtained from reaction  $\text{Fe}^{2+} + 4 \text{cysteine} + \text{NO}$  at pH 7 and 55 °C.
- Figure 7.** Raman spectra of a mixture of a mixture of (A)  $\text{HSO}_3^-/\text{SO}_3^{2-}$  at pH 7; (B) cystine/ $\text{ClO}_4^-$ ; and (C)  $\text{HSO}_3^-/\text{SO}_3^-$  with cystine/ $\text{ClO}_4^-$  at pH 7.



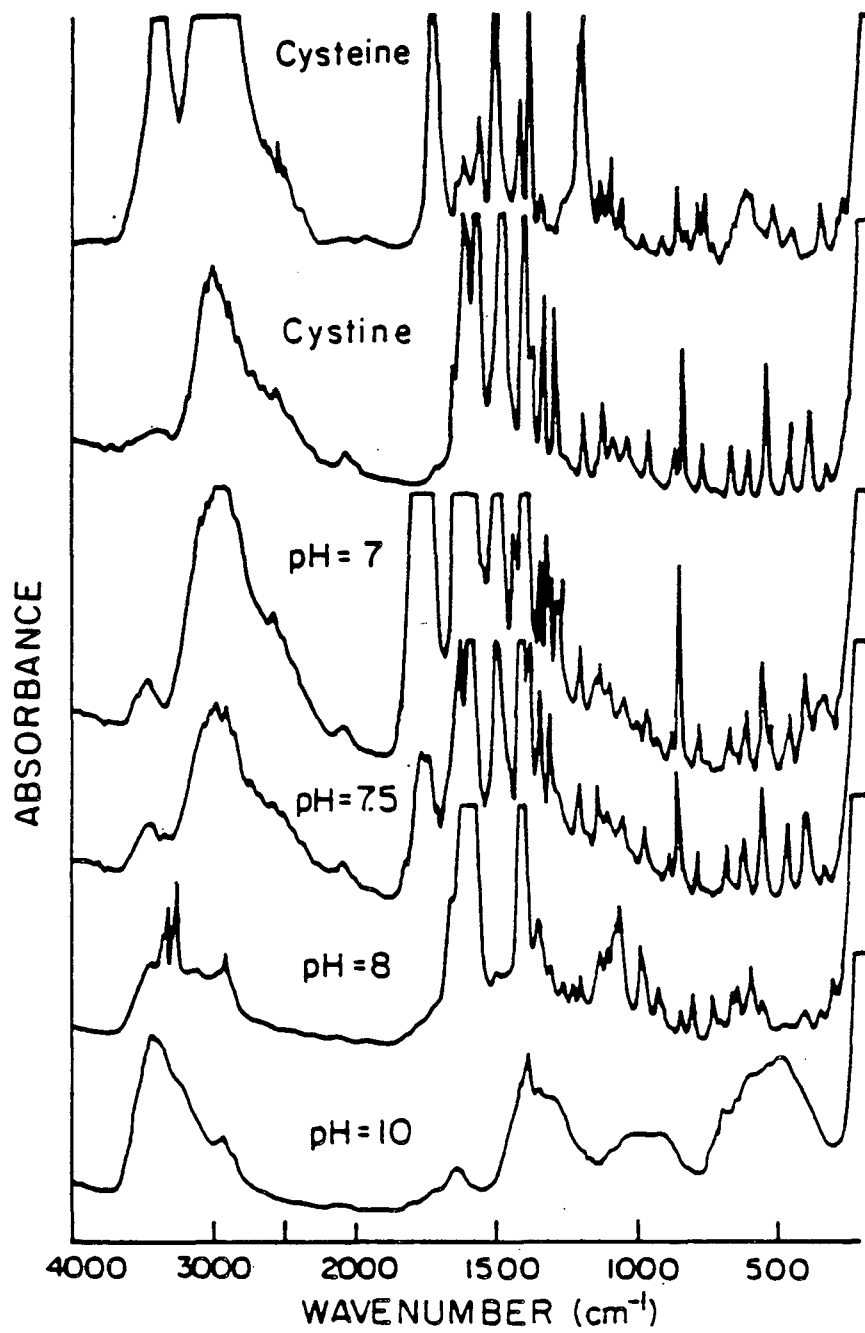
XBL863-7581

Fig. 1



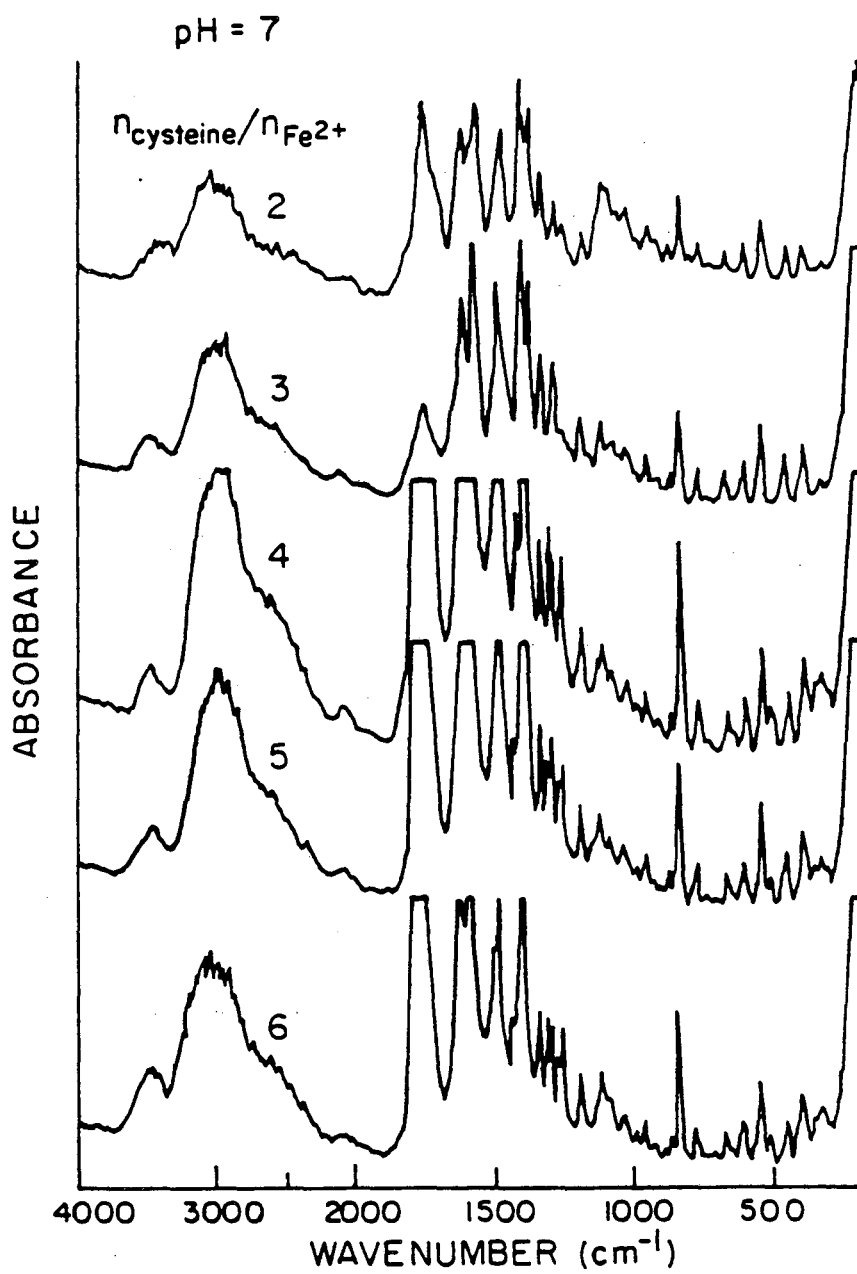
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Fig. 2



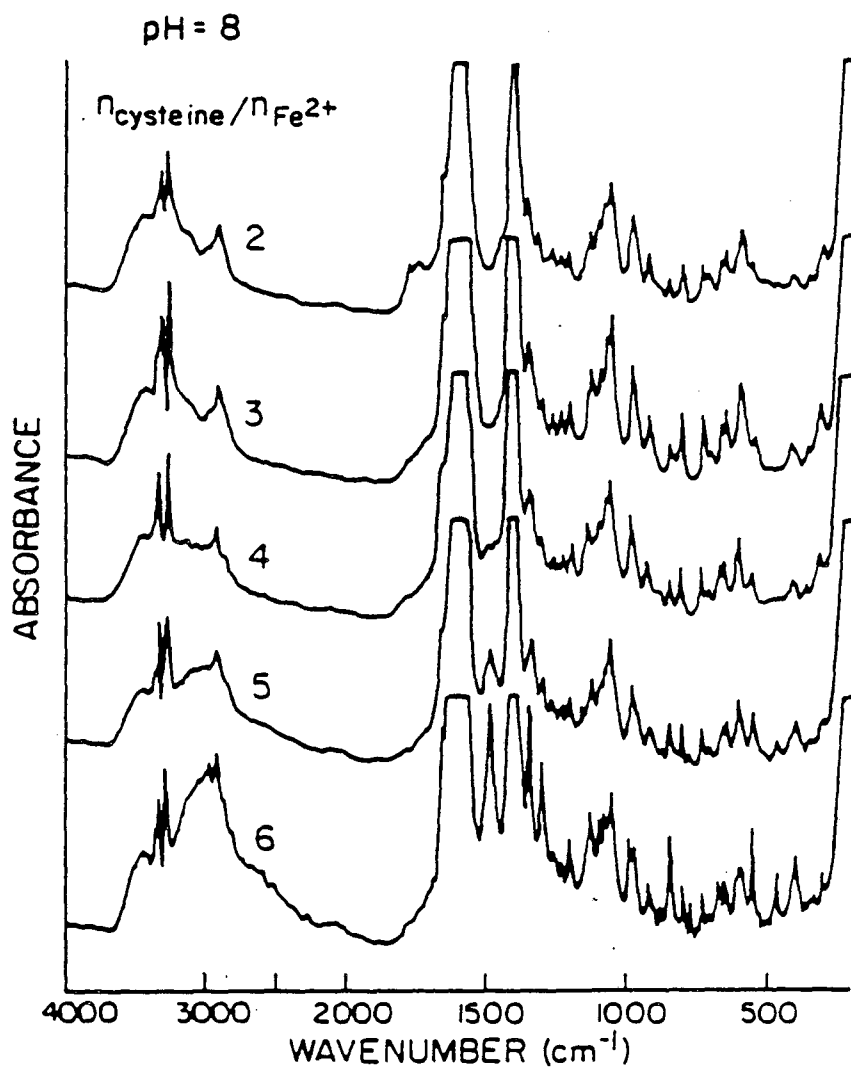
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Fig. 3



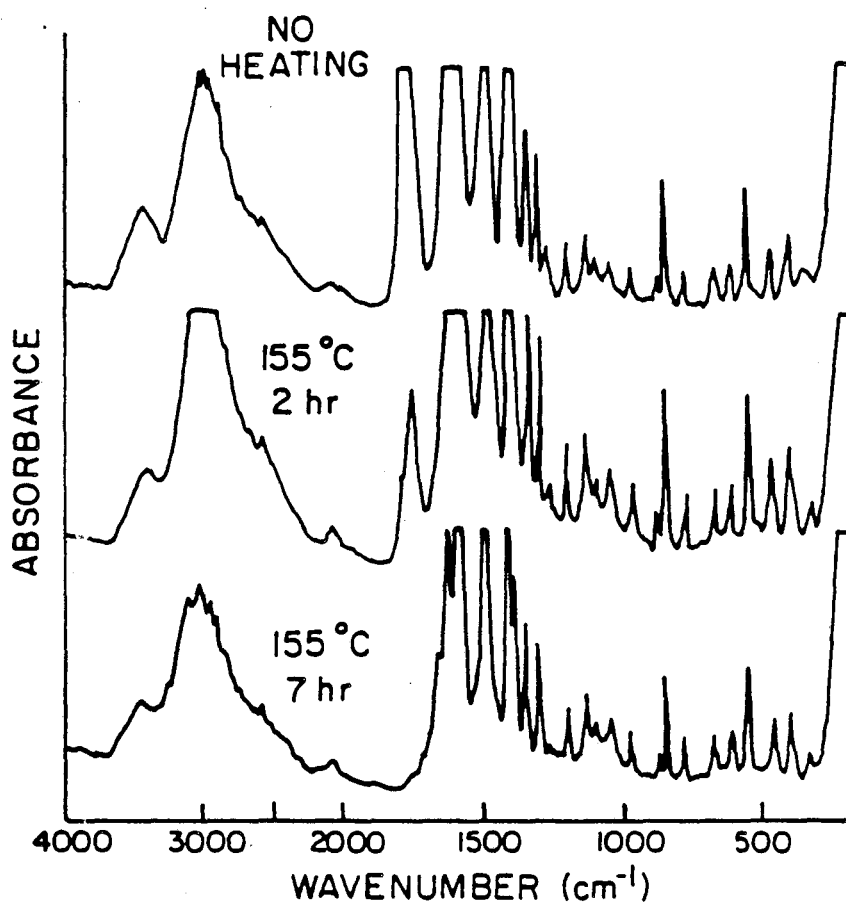
XBL 863-7584

Fig. 4



XBL863-7385

Fig. 5



XBL 863-7586

Fig. 6

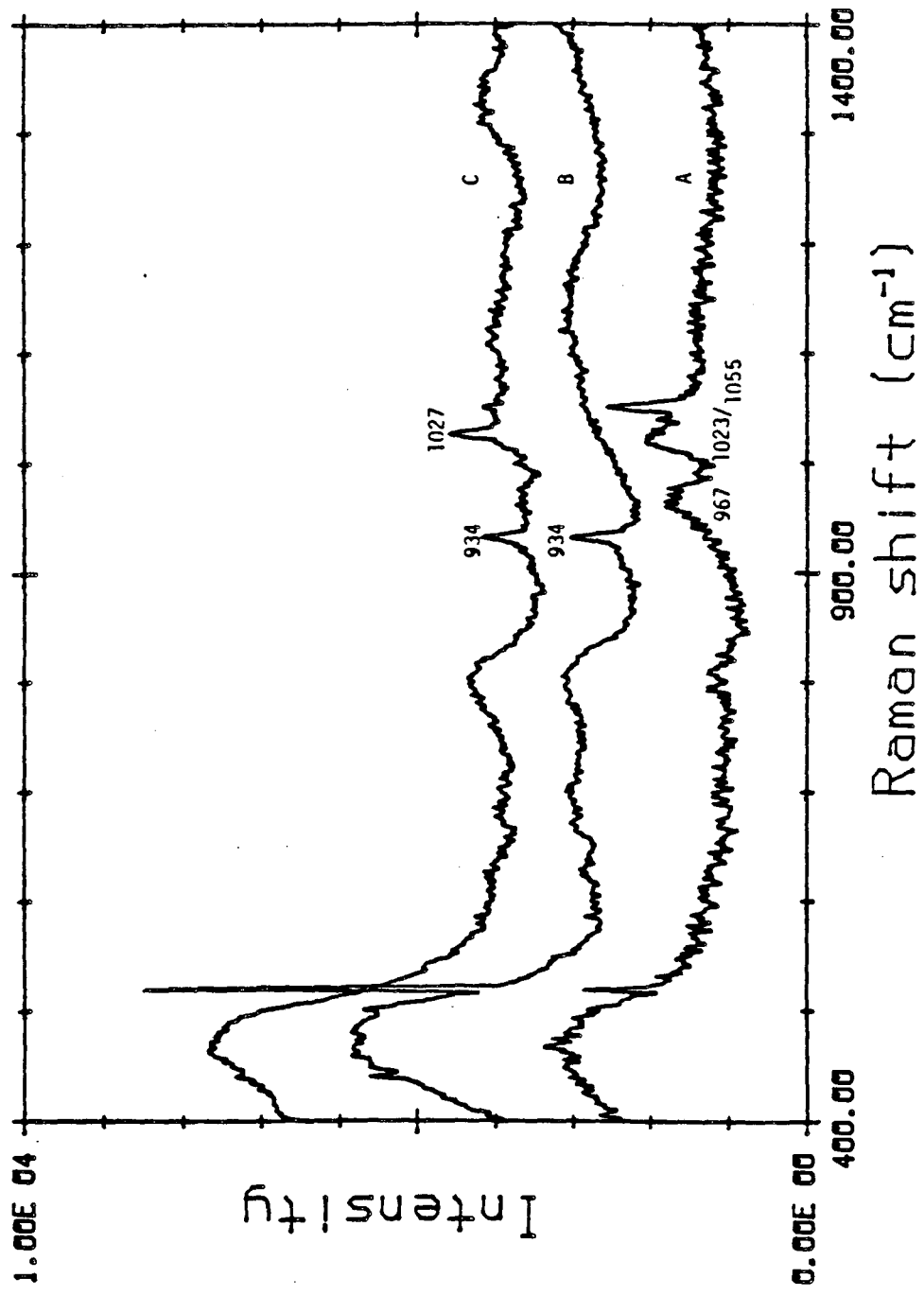


Fig. 7



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