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### Publication Date

1989-07-01

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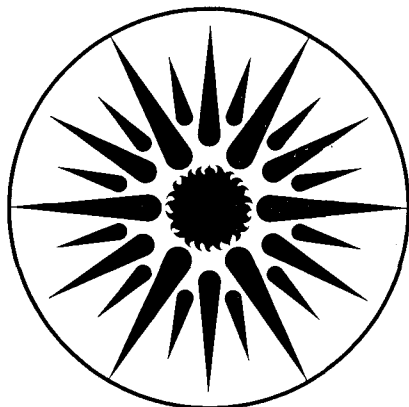
## APPLIED SCIENCE DIVISION

Submitted to Nature

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July 1989



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## A Simple Scrubber for Removing Nitrogen and Sulfur Oxides from Waste Gas

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Sulfur and nitrogen oxides emitted by the combustion of fossil fuels in power plants play an important role in acid rain production.<sup>1</sup> Most of the flue gas desulfurization (FGD) scrubbers installed to date involves wet limestone processes which are efficient in SO<sub>2</sub> control but are incapable of removing nitric oxide. We report herein a new and efficient method for the combined removal of SO<sub>2</sub> and NO<sub>x</sub> from flue gas using aqueous emulsions containing yellow phosphorus and an alkali. The products comprise of sulfate, nitrate, and phosphate salts which can be used as fertilizer materials. The process described here may also be applied to stationary sources other than power plants, such as smelters, nitric acid plants, and municipal incinerators for NO<sub>x</sub> control.

The role of sulfur and nitrogen oxides in acid rain formation and the destruction of lakes and forest ecosystems has been established.<sup>2,3</sup> More stringent regulations of these emissions from both mobile and stationary sources are therefore imminent. The development of efficient processes for simultaneous SO<sub>2</sub> and NO<sub>x</sub> control for power plants flue gas is particularly important since fossil fuel-fired steam boilers represent a major source of sulfur and nitrogen oxide emissions. Existing wet FGD scrubbers in power plants are incapable of removing flue gas NO because of its low solubility in water. Several methods have been developed to enhance NO absorption in these scrubbers, including the use of oxidants to oxidize NO to the more soluble NO<sub>2</sub><sup>4</sup> and the addition of various iron (II) chelates to bind and activate NO.<sup>5-10</sup> So far, none of these methods has been

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demonstrated to be cost-effective despite high removal efficiencies of both  $\text{SO}_2$  and  $\text{NO}_x$ . In our continuing effort to search for new additives for scrubbing flue gas NO, we have discovered that aqueous emulsions containing yellow phosphorus ( $\text{P}_4$ ) and an alkali such as limestone ( $\text{CaCO}_3$ ) can be used to remove up to 100% NO and  $\text{SO}_2$  in a simulated flue gas stream.

The removal of NO from flue gas by aqueous yellow phosphorus emulsions was studied using a bench-scale gas scrubber. In a typical experiment, 1.0 g yellow phosphorus was melted in 0.2 l water at 60 °C in a Pyrex reaction column (50 mm i.d. x 210 mm). A fine yellow phosphorus dispersion was created when a simulated flue gas stream (~500 ppm NO, 4%  $\text{O}_2$ , and the balance  $\text{N}_2$ ) was bubbled through the reactor at a flow rate of ~0.9 l min<sup>-1</sup>. The scrubbed flue gas was passed through a gas washing bottle containing 0.2 M NaOH, and the NO and  $\text{NO}_2$  concentrations in the exit gas were monitored by a Thermoelectron Model 14A chemiluminescent  $\text{NO}_x$  analyzer. The compositions of the spent scrubbing liquor and the NaOH absorbing solution were determined using a Dionex 2101i ion chromatograph.

The important finding that flue gas NO can be effectively scrubbed by an aqueous yellow phosphorus emulsion is shown in Figure 1. We found that the presence of  $\text{O}_2$  is essential for the NO removal, and that the system is more effective in the presence of excess  $\text{O}_2$  in flue gas. The gradual decline of NO removal efficiencies as a function of time is attributed to the increasing acidity of the scrubbing liquor and can be eliminated by the addition of an alkali to the system (see Figure 2). Ion chromatographic analyses of the spent scrubbing liquor and the NaOH absorbing solution showed that all the NO absorbed was converted to a mixture of nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^-$ ), and that >95% of the  $\text{P}_4$  consumed can be recovered as a mixture of hypophosphite ( $\text{H}_2\text{PO}_2^-$ ), phosphite ( $\text{H}_2\text{PO}_3^-$ ), and phosphate ( $\text{H}_2\text{PO}_4^-$ ).

The simultaneous removal of NO and SO<sub>2</sub> from flue gas can be accomplished by the addition of limestone to the phosphorus emulsion, as shown in Figure 2. The experiment was performed using a ~1.2 l jacketed reactor containing 0.9 l of a 0.3% w/w phosphorus/5.0% w/w CaCO<sub>3</sub> slurry. The simulated flue gas was composed of 560 ppm NO, 2900 ppm SO<sub>2</sub>, 10% O<sub>2</sub>, and the balance was N<sub>2</sub>. In this case, up to 100% of the flue gas NO and SO<sub>2</sub> can be removed. The solid collected from the scrubber after the reaction was shown by laser Raman spectroscopy to contain gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), CaCO<sub>3</sub>, and P<sub>4</sub>. The liquid phase in both the scrubber and the absorber were determined by ion chromatography to contain SO<sub>3</sub><sup>=</sup>, SO<sub>4</sub><sup>=</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, H<sub>2</sub>PO<sub>2</sub><sup>-</sup>, H<sub>2</sub>PO<sub>3</sub><sup>-</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, as shown in Figure 3. In addition, the production of the nitrogen-sulfur compounds hydroxyimidodisulfate (HIDS) and imidodisulfate (IDS) in the scrubbing liquor were confirmed by ion chromatography.<sup>11</sup> Both HIDS and IDS were subsequently hydrolyzed to NH<sub>4</sub><sup>+</sup> when the scrubbing liquor was acidified to pH < 2. The formation of nitrogen-sulfur compounds via the reaction between NO<sub>2</sub><sup>-</sup> and HSO<sub>3</sub><sup>-</sup> in scrubbing liquor and their hydrolysis reactions have been reported previously.<sup>5,12</sup> Therefore, the use of yellow phosphorus for combined NO and SO<sub>2</sub> removal can result in the production of sulfate, nitrate, and phosphate salts of calcium or ammonium, all of which are valuable chemicals for the manufacture of fertilizers.<sup>13</sup>

The effectiveness for NO removal by yellow phosphorus was measured in a closed reaction system. A 1.0 l round bottom flask containing 0.25 mg P<sub>4</sub>, 0.1 g CaCO<sub>3</sub>, and 60 ml deionized H<sub>2</sub>O was evacuated and refilled with 1 atm of a gas mixture consisting of 500 ppm NO, 10% O<sub>2</sub>, and the balance N<sub>2</sub>. The reaction mixture was stirred magnetically at 50 °C until all phosphorus has been consumed (~4 h). The composition of the reaction mixture was analyzed periodically by ion chromatography to determine the NO removal effectiveness as defined by

$$P/NO = \frac{[H_2PO_2^-] + [H_2PO_3^-] + [H_2PO_4^-]}{[NO_2^-] + [NO_3^-]}$$

Our results showed that a P/NO ratio of 0.5 was obtained throughout the 4 h period. Control experiments without yellow phosphorus indicated that NO removal via oxidation by O<sub>2</sub> to form NO<sub>2</sub> accounted for <10% of the total NO removed when yellow phosphorus was present. When 0.92 mM HSO<sub>3</sub><sup>-</sup> (corresponding to ~3,000 ppm flue gas SO<sub>2</sub>) was added to the above reaction mixture, a P/NO ratio of 0.8 was obtained.

A mechanism for NO removal by yellow phosphorus can be proposed. It is well known that phosphorus vapor reacts with oxygen gas in the presence of moisture to give various phosphorus oxides, oxygen atom, and ozone.<sup>14-16</sup> The O and O<sub>3</sub> thus produced can oxidize NO to NO<sub>2</sub>, which can then react with another molecule of NO to form N<sub>2</sub>O<sub>3</sub> or dimerize to form N<sub>2</sub>O<sub>4</sub>. Both N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>4</sub> are much more soluble in water than NO, and the HNO<sub>2</sub> and HNO<sub>3</sub> produced upon the hydrolysis of N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>4</sub> are neutralized by alkali present in the scrubbing liquor (e.g. CaCO<sub>3</sub>) to yield NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>. The mechanism for the oxidation of phosphorus to various phosphorus oxides appears to be complicated<sup>14-16</sup> and is presently under investigation.

A preliminary economic consideration of the above phosphorus-based process has been carried out, suggesting that the technology warrants further development. The addition of yellow phosphorus to a limestone FGD system to achieve simultaneous control of NO<sub>x</sub> emissions does not require excessive additional equipments, since the processing of the scrubbing liquors appears to be rather straightforward. The recovery of phosphorus by-products can be achieved simply by precipitation at appropriate pH of the liquors. At the operating pH of a limestone scrubber (between 3.5 and 5.5), the majority of phosphate is

in the form of  $\text{H}_2\text{PO}_4^-$ . The calcium salt  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  is relatively water-soluble under such conditions and can be separated from less soluble  $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  by simple filtration. Limestone can then be added to the filtrate to raise the pH to 8 or higher where  $\text{H}_2\text{PO}_4^-$  is converted to  $\text{HPO}_4^{2-}$ . The calcium salt  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  is quite insoluble under such conditions and can be recovered as a precipitate. Therefore, much of the value of yellow phosphorus ( $\$0.91/\text{lb}$ )<sup>17</sup> consumed can be recovered as  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , which is a valuable commercial product used as animal feed and fertilizer ( $\$0.63/\text{lb}$  of P)<sup>17</sup>. At a P/NO ratio of 1, the loss in the value of phosphorus reagent ( $\$560$  per ton of NO removed) is small compared to the cost of a selective catalytic reduction (SCR) process<sup>18</sup>. With an improvement of P/NO ratio, this loss in chemical value can be further reduced. The soluble nitrogen-sulfur compounds formed in the system can be removed from the solutions either by precipitation as potassium salts or by acid hydrolysis.<sup>5,12</sup> A scale-up test of this phosphorus-based process is being conducted on a 20-acfm bench-scale system, and a realistic economic evaluation of a commercial plant design will follow the conclusion of future integrated pilot-scale tests.

In summary, we have discovered a new approach for the efficient removal of flue gas NO and SO<sub>2</sub> in a single scrubbing system. This could provide a cost-effective alternative to commercial SCR processes in which separate scrubbers for SO<sub>2</sub> and NO<sub>x</sub> removal are required.

**Acknowledgement.** This work was supported by the Assistant Secretary of Fossil Energy, Office of Coal Utilization Systems, US Department of Energy under Contract No. DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, PA.



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## Figure Captions

- Figure 1. NO removal by yellow phosphorus emulsions as a function of O<sub>2</sub> partial pressure in flue gas. The reactions were carried out at 60 °C, and the initial and final pH were 3.5 and 1.5, respectively. The simulated flue gas contained 500 ppm NO, 0-20% O<sub>2</sub>, and the balance was N<sub>2</sub>.
- Figure 2. Combined NO and SO<sub>2</sub> removal using an aqueous emulsion containing 0.8% w/w P<sub>4</sub> and 5.0% w/w CaCO<sub>3</sub>. The reaction was performed at 55 °C, and the initial and final pH were 7.5 and 4.2, respectively. The simulated flue gas contained 560 ppm NO, 2900 ppm SO<sub>2</sub>, 20% O<sub>2</sub>, and the balance was N<sub>2</sub>.
- Figure 3. Ion chromatograms of 25x diluted spent scrubber and absorber solutions from the combined NO and SO<sub>2</sub> removal experiment with P<sub>4</sub>/CaCO<sub>3</sub>. A Dionex 2101i ion chromatograph equipped with a conductivity detector and a Dionex AS4 anion separation column were used for the analyses. The eluants were: (a) 5.3 mM Na<sub>2</sub>CO<sub>3</sub>; and (b) 4.0 mM Na<sub>2</sub>CO<sub>3</sub>/2.0 mM NaOH/0.5% v/v CH<sub>3</sub>CN.

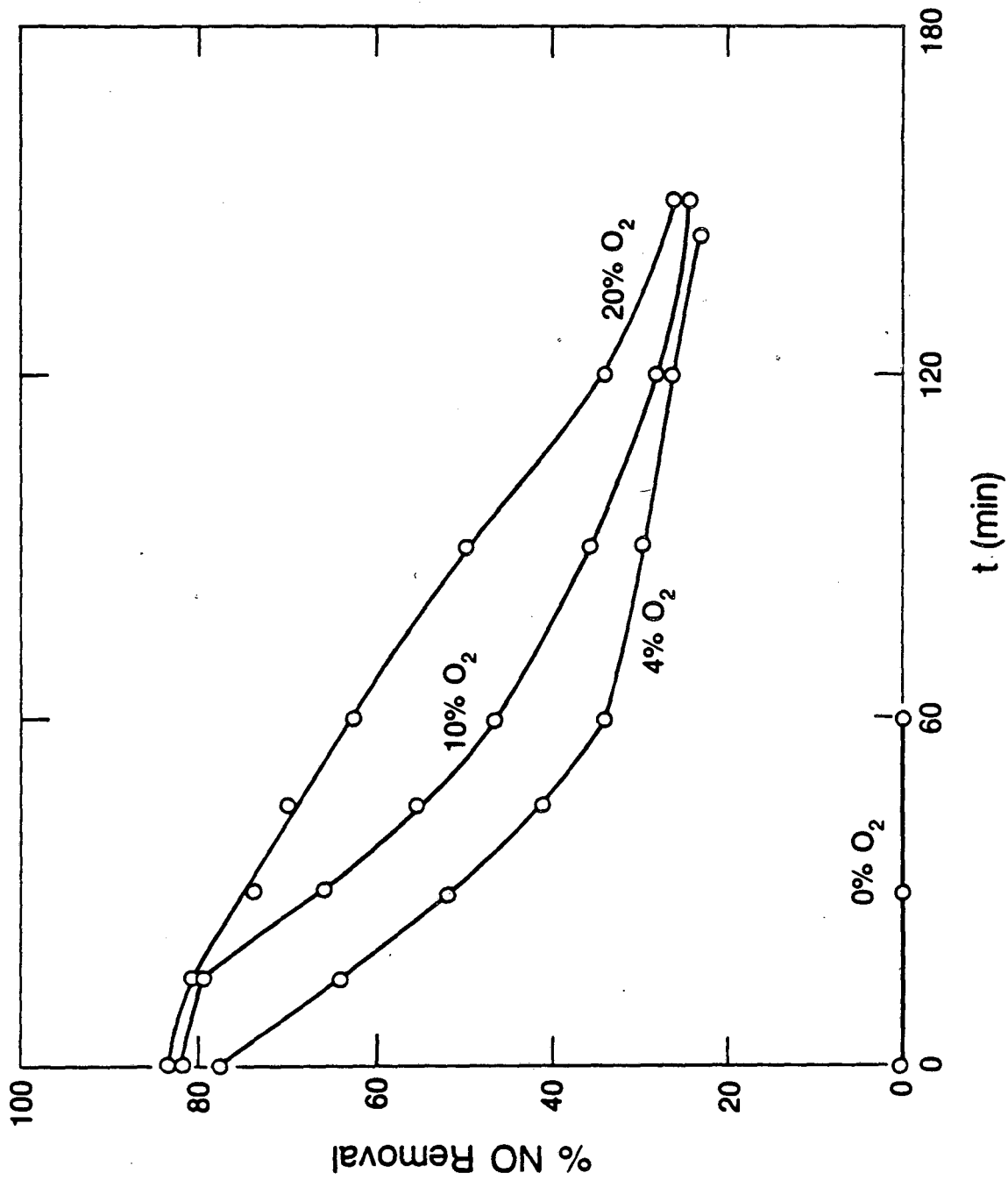


Fig. 1

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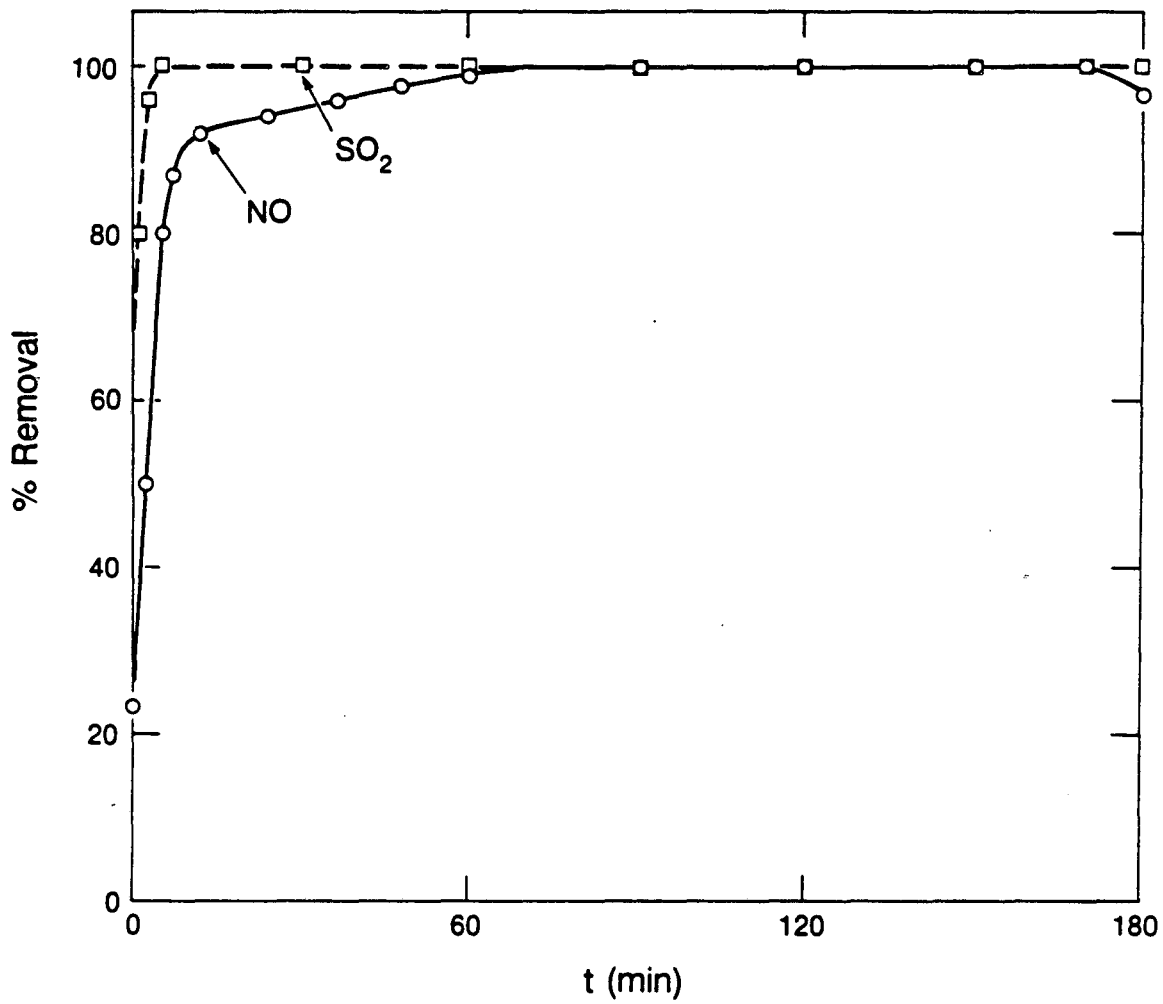


Fig. 2

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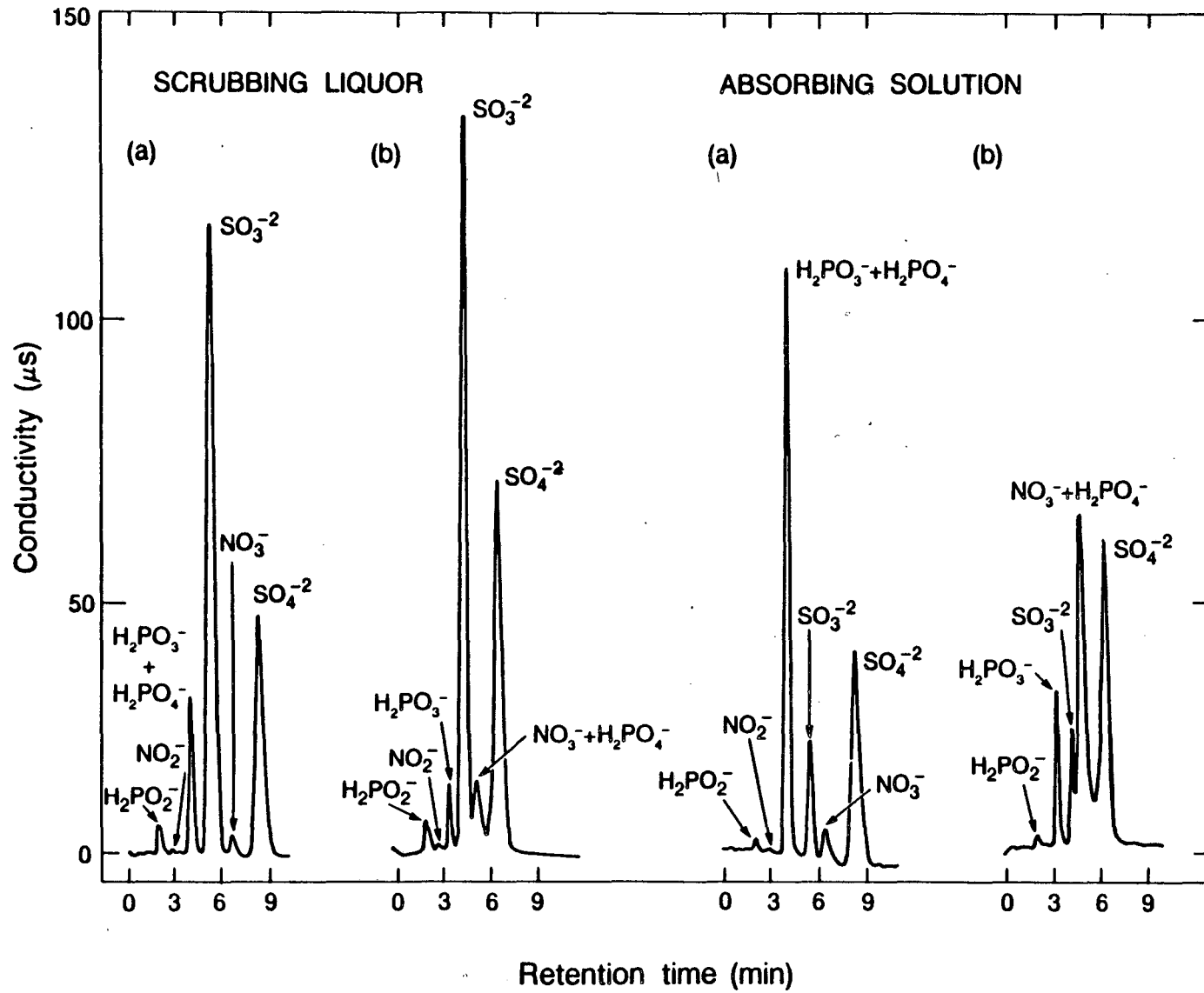


Fig. 3

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