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Authors

Littlejohn, D.

Chang, S.G.

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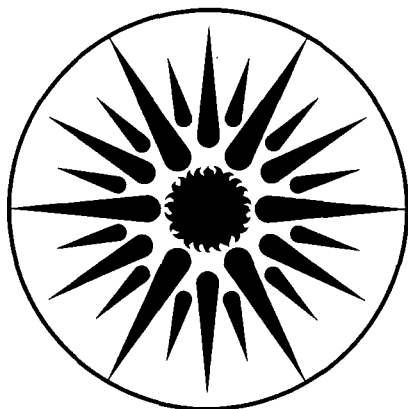
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April 1985

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Determination of Nitrogen-Sulfur Compounds by Ion Chromatography

D. Littlejohn and S. G. Chang*

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720
(415) 486-5125

ABSTRACT

Ion chromatography was used in the determination of hydroxyimidodisulfate, hydroxysulfamate, imidodisulfate and N-nitrosohydroxylamine-N-sulfonate. 1.5 mM bicarbonate was used as an eluent with a standard separation column for separation of the singly-charged anions. 12 mM or 18 mM carbonate was used as an eluent with a short separation column for separation of the doubly-charged anions. The detection limits for these compounds were as follows: hydroxyimidodisulfate 7.4×10^{-6} M, hydroxysulfamate 0.5×10^{-6} M, imidodisulfate 1.4×10^{-6} M, N-nitrosohydroxylamine-N-sulfonate 14×10^{-6} M. Ion chromatography was found to have an advantage in speed and sensitivity compared to other determination methods.

A number of nitrogen-sulfur compounds can form in aqueous solutions of nitrogen oxyanions and sulfur oxyanions.^{1,2} Conditions suitable for their formation exist in wet flue gas scrubbers and aqueous aerosols in polluted air. The nitrogen sulfonates of interest in this study are hydroxyimidodisulfate (HIDS), hydroxysulfamate (HSA), nitrido-trisulfate (NTS), imidodisulfate (IDS), and N-nitroso-hydroxylamine-N-sulfonate (NHAS). They are shown in Fig. 1 with some of the reactions they undergo in aqueous solutions.

Three techniques have been previously described for the determination of some of these compounds. The gravimetric and iodometric technique developed by Sato *et al.*³ requires a series of treatments of a sample to obtain the amounts of HIDS, NTS and IDS present. They gave no method for HSA or NHAS determination. Oblath⁴ used a method where HIDS was oxidized to nitrosodisulfonate ($\text{ON}(\text{SO}_3^-)_2$) and colorimetry was done to determine nitrosodisulfonate. This technique also involves a number of steps. Raman spectrometry permits simultaneous determination of all of the compounds listed above and requires a very small sample volume.⁵ It eliminates the need for extensive manipulation of the sample. The major limitation of Raman spectrometry is lack of sensitivity. Samples with low concentrations (0.001-0.01 M) of the compounds of interest require very long data acquisition times. Determination of these compounds by ion chromatography has been found to combine high sensitivity and rapid measurement times.

Experimental Section

Apparatus. A Dionex 2010i ion chromatograph equipped with a Dionex AG4 guard column, a Dionex AS4 anion separation column, and a Dionex anion fiber suppressor column was used. For determination of HSA and sulfamate, 1.5 mM bicarbonate eluent was used with a flow rate of 2.0 mL/min at a pressure of 700-800 psi. For determination of HIDS, IDS and NHAS, the AG4 column alone was used as the separation column with 12 mM or 18 mM carbonate eluents. The flow rate was 1.5 mL/min at a pressure of 200-300 psi. A 50 μL sample loop volume was used. For conductivity suppression, 0.025 N H_2SO_4 was used with a flow rate of 2.5-3.5 mL/min for the 1.5 mM eluent and a flow rate of 5-7 mL/min for the 12 mM and 18 mM eluents. A Dionex conductivity detector was used. All

columns were at ambient temperature (20-25 °C) and temperature regulation was not required.

Reagents. Eluents were prepared from reagent grade sodium carbonate or sodium bicarbonate and doubly deionized water. Sulfuric acid for suppression was prepared by diluting concentrated sulfuric acid with doubly deionized water. The NTS and IDS for standard solutions were synthesized by the procedure given by Sisler and Audrieth.⁶ HIDS was prepared by the method of Rollefson and Oldershaw.⁷ HSA was prepared by the method given by Oblath.⁴ The potassium salts of the above compounds were stored in a vacuum desiccator at 5 °C until solutions were needed. Solutions of these compounds were treated with sufficient concentrated NaOH to make the solutions alkaline. NHAS solutions were prepared on a vacuum line just prior to use, following the method of Nunes and Powell.⁸

Results and Discussion

An ion chromatogram of a mixture of IDS, HIDS and NHAS is shown in the bottom half of Fig. 2. The chromatogram was recorded on the 10 μ S scale. The peak present at $\Delta t \approx 1$ min is due to sulfate impurity. An eluent flow rate of 1.5 mL/min was used to avoid overloading the suppressor column. The background conductivity was typically 35-40 μ S when operating under these conditions. An ion chromatogram of a mixture of sulfamate and HSA is shown in the top half of Fig. 2. This chromatogram was also recorded on the 10 μ S scale. A small amount of fluoride impurity is present as a peak at $\Delta t \approx 2$ min. An eluent flow rate of 2.0 ml/min was used and the background conductivity was 13-17 μ S.

It was not possible to make determinations of NTS with the column used in these studies because it is very strongly retained on the column. In the alkaline conditions of carbonate and bicarbonate eluents, NTS has a 3- charge. HSA and sulfamate have 1- charges and will pass through the 5 cm guard column and 25 cm separation column in a few minutes using a low concentration eluent. IDS, HIDS and NHAS have 2- charges and require a high concentration eluent to pass through the 5 cm guard column alone in a

few minutes.

To transport a compound with a 3- charge through a column with this type of ion exchange resin in a reasonable time would require an excessively high eluent concentration. A resin that would work well with NTS would be unlikely to separate the other compounds.

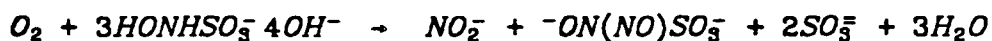
As indicated in Fig. 1, these compounds can hydrolyze in aqueous solutions.² Generally, they are stable in alkaline solutions, although NHAS and HSA susceptible to attack by oxygen.⁹ There is considerable variation in the rates of hydrolysis for these compounds. For a given pH and nitrogen sulfonate concentration, the relative hydrolysis rates, in increasing order, are: HSA, IDS, HIDS, NTS and NHAS. Since NTS hydrolyzes much more easily than IDS, it can be converted into IDS for measurement by ion chromatography. A sample can be run on the ion chromatograph to determine IDS, acidified to pH 2-3 and allowed to stand 5-10 minutes, and run again to measure the increase in IDS concentration. Tests done with standard solutions indicate this is a quantitative method.

It was found that determinations of nitrogen-sulfur compounds in samples were best done by comparison with standard solutions. Ion chromatograms of dilutions of freshly prepared alkaline solutions of the compounds were run either prior to or following chromatograms of solutions containing unknown amounts of the compounds. This minimized the influence of variations in the ion chromatograph operating parameters. The linearity of the ion chromatograph's response to the compounds was checked by measuring the peak heights obtained from a range of sample concentrations. The highest concentrations injected were 1×10^{-3} M. Fig. 3 shows a plot of peak height vs concentration for HSA and sulfamate. Both compounds significantly deviate from linearity above 2×10^{-4} M. The peaks become broader and shorter than what would be expected from extrapolation of the peak heights obtained at lower concentration. Fig. 4 shows a plot of peak height vs concentration for IDS, HIDS and NHAS. IDS deviated from linear response above 2×10^{-4} M concentration, while HIDS and NHAS exhibited good linearity up to 6×10^{-4} M concentration. All compounds exhibited broadening of the

peaks at the highest concentrations tested. Also, when the AG4 column alone was used, reduction in the compounds' retention time was noted at high concentrations ($\sim 1 \times 10^{-3}$ M).

Detection limits for the compounds were obtained where the detection limit was defined as the concentration that generated a peak with a height twice that of the background noise. The detection limits obtained are as follows: HSA : 0.5×10^{-6} M, sulfamate : 0.6×10^{-6} M, IDS : 1.4×10^{-6} M, HIDS : 7.4×10^{-6} M, NHAS : 12×10^{-6} M. As the retention time of a compound increases, the peak broadens and decreases in height. Thus, it is advantageous to have as short a retention time as possible within the limitations of obtaining separation between the peaks of chromatogram.

In some instances, there was overlap between the HSA peak and the Cl^- peak in samples containing both of these anions. The simplest way to correct the overlap was found to make the solution alkaline ($\text{pH} \gtrsim 10$) and to pass oxygen through for about 10 minutes to oxidize the HSA. The Cl^- peak could then be obtained free of interference and then be used to correct the HSA peak obtained initially to determine HSA. The HSA is oxidized as follows⁹:



Besides the hydrolysis reaction shown in Fig. 1, NHAS, can react with oxygen to form NO_2^- and SO_4^{2-} . Since SO_3^{2-} oxidizes readily and the amount of NHAS that is converted to NO_2^- is variable, neither NO_2^- or SO_3^{2-} can be used reliably to determine HSA.

The ion chromatographic method has been used to observe reactions involving nitrogen sulfonates. It has also been used to determine these compounds in flue gas scrubbing liquors. The short time needed for measurements minimizes the possibility of decomposition during the determination procedure.

Acknowledgements

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

Credit

This work was supported by the Assistant Secretary for Fossil Energy, Office of Coal Research, Advanced Environment Control Division of the U.S. Department of Energy under contract number DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, Pennsylvania.

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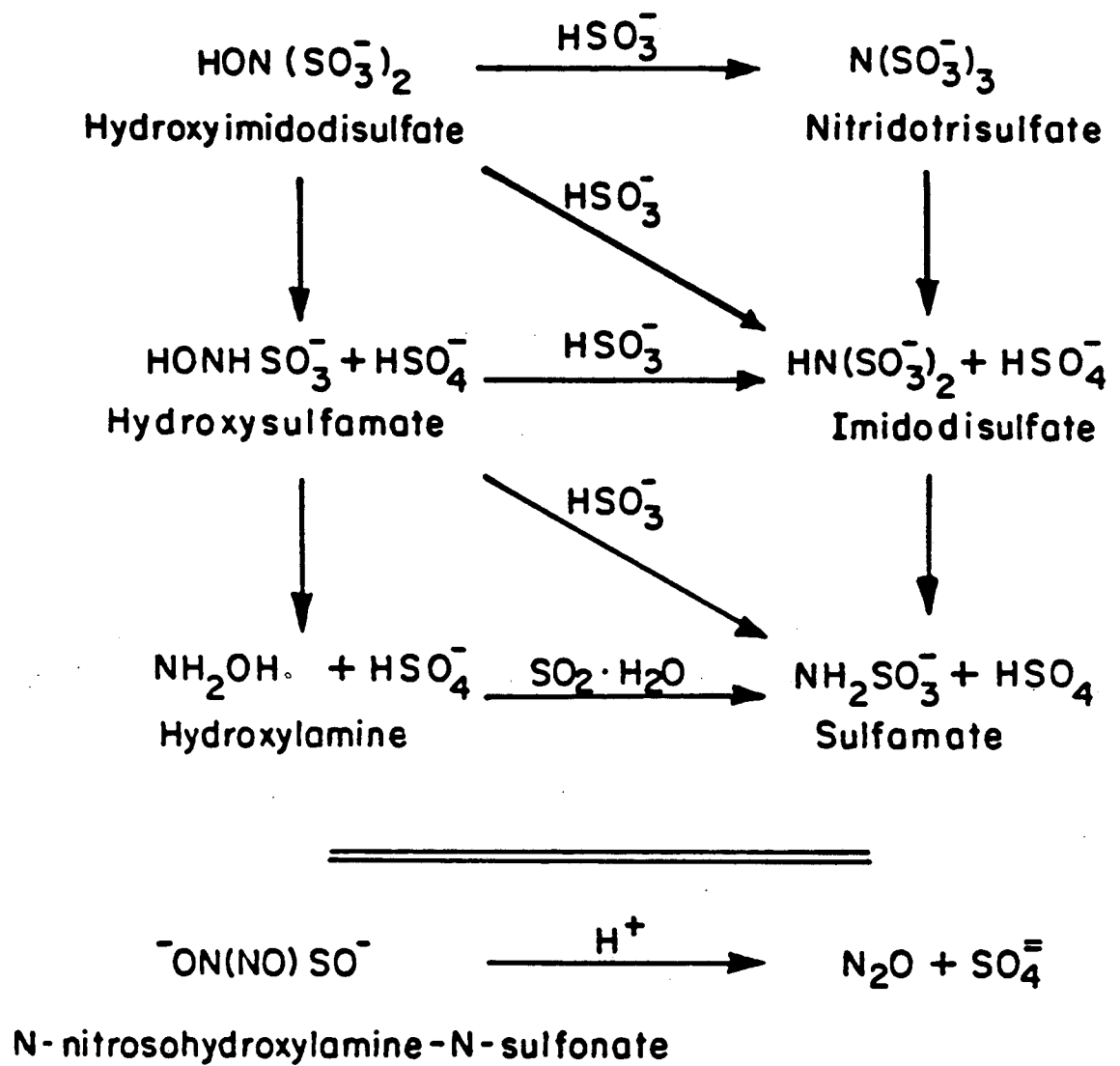
FIGURE CAPTIONS

Figure 1 Reactions of nitrogen-sulfur compounds.

Figure 2 (upper) Ion chromatogram of sulfamate and hydroxysulfamate. (lower) Ion chromatogram of imidodisulfate, hydroxyimidodisulfate and N-nitrosohydroxylamine-N-sulfonate.

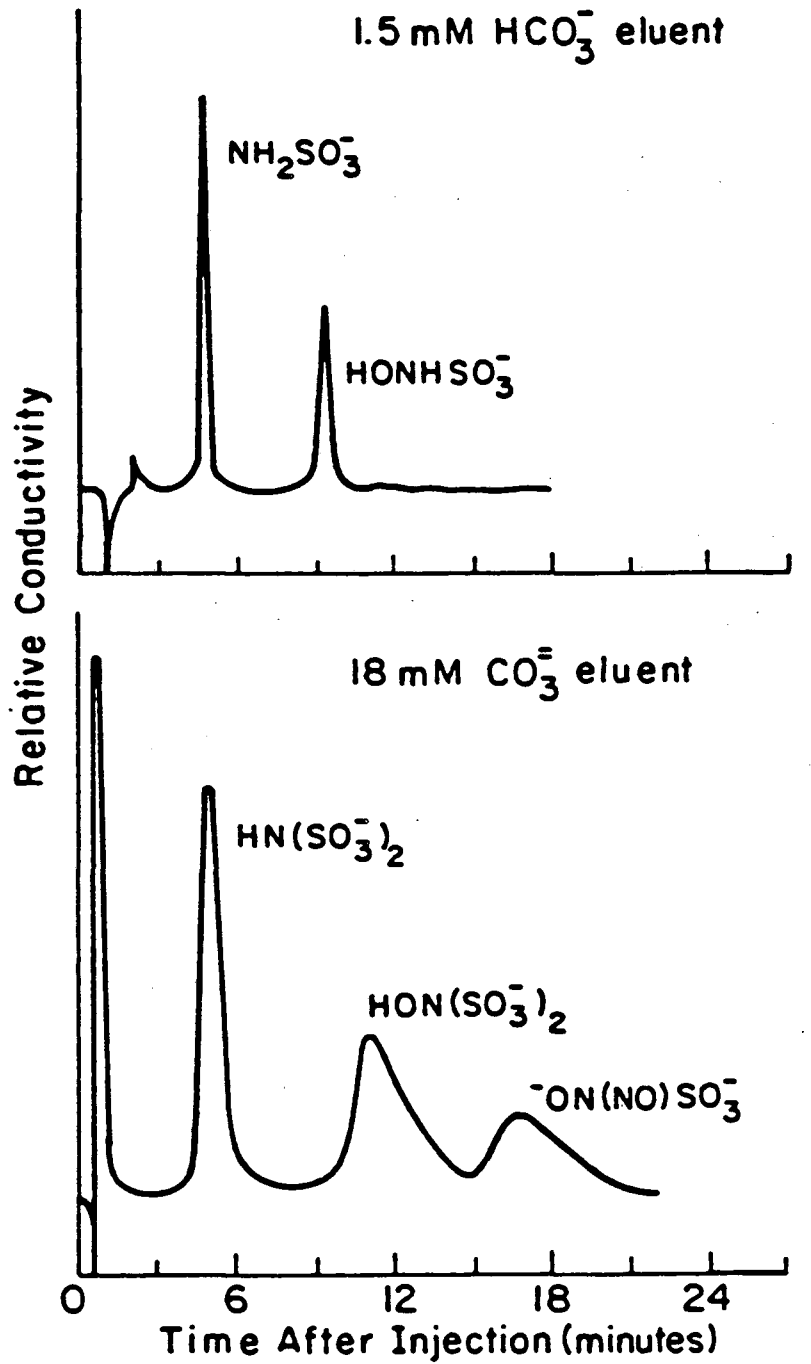
Figure 3 Calibration curve for sulfamate and hydroxysulfamate.

Figure 4 Calibration curve for imidodisulfate, hydroxyimidodisulfate and N-nitrosohydroxylamine-N-sulfonate.



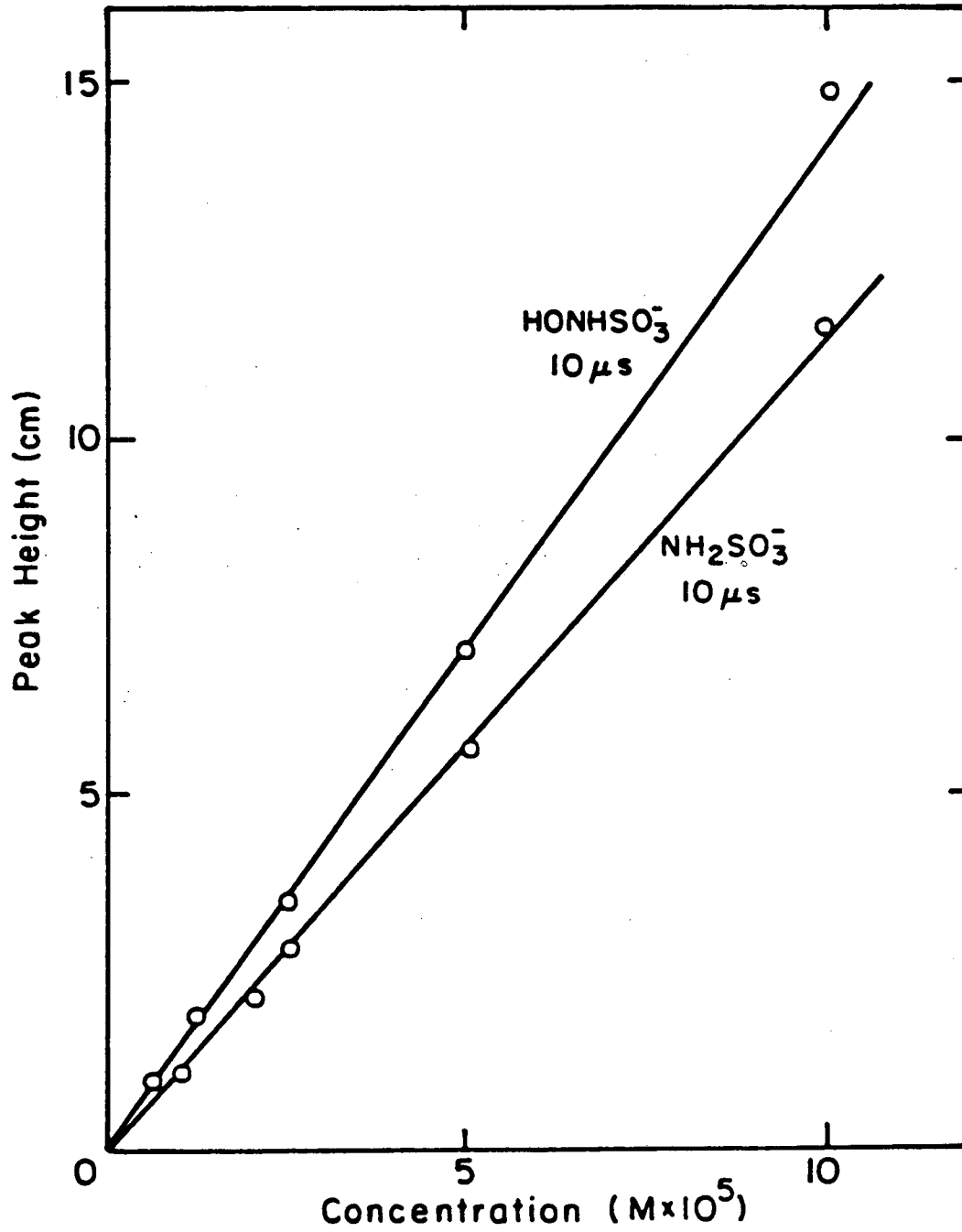
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Fig. 1



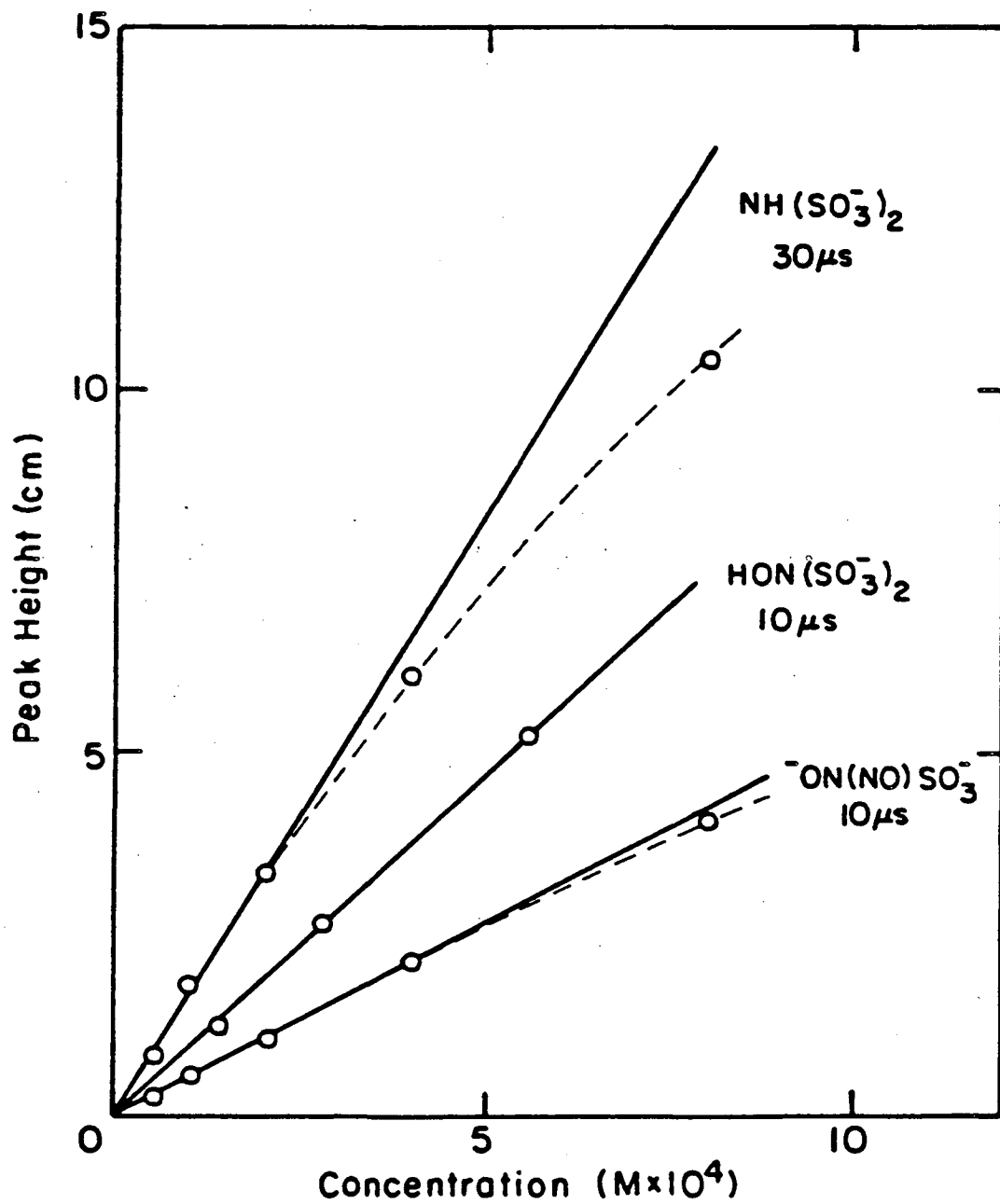
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Fig. 2



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Fig. 3



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Fig. 4

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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