Effect of Manganese Additives on NO-Emissions from a Small Laboratory Oil Burner

Elmar R. Altwicker, Ira S. Brodsky, and Thomas T. Shen

Rensselaer Polytechnic Institute, Troy, N. Y. and New York State Department of Environmental Conservation, Albany, N. Y.

Introduction Many techniques for emission reduction from oil fired installations can be cited. These include[1] 1) operating procedures; 2) fuel selection; 3) design and installation; 4) combustion modifications; 5) new combustion procedures; 6) additives. Although additives are in use to some extent, there is little evidence of reliable performance for the lowering of pollutant emissions.

There is even less information on or understanding of the effect of oil additives on levels of NO_x-emissions from oil diffusion flames. Such understanding is of interest since small installations that burn #2 distillate fuel oil form a large group of sources in urban areas which emit near ground level. Control techniques other than burner modifications, new furnace and burner design, or additives are unlikely to be of commercial importance for these sources. We have previously reported on combustion studies which utilized a small-scale atomizing burner and distillate fuel oil, and some indications of the effect of metallic and nonmetallic additives on nitric oxide emissions, which were marginal[2,3]. The results of extensive evaluations of several chemical compounds and commercial formulations have been published and it was concluded that none of the compounds investigated showed an effect on the nitric oxide level[4]. A detailed review on available data has recently appeared[5].

The reactions whereby an additive might lower NO_x-levels observed in the stack gases are unknown but could be basically of three types: 1) the additive interferes with reactions leading to NO-formation; 2) the additive catalyzes NO-decomposition; 3) the additive affects only NO_x-formation from fuel nitrogen.

Experimental Since small burners were not available commercially, it was necessary to construct a burner that met the requirements for our laboratory investigations, i.e. low total oil and air flow, in order to facilitate the frequent switch between oil flow for baseline data and oil flow for additive studies. The final assembly of the burner system is shown in Figure 1. Details of second experimental burner are shown in Figure 2.

The operating conditions of the burner system for each test were kept constant. Fuel flow rate was adjusted to 3.0 ± 0.1 grams per minute; combustion air flow was 37.7 liters per minute (5.1 liters per minute of this was primary air flow); a slight excess of air was used corresponding to $\emptyset = 0.96$, based on an ultimate analysis of the fuel. The burner was stabilized for 30 minutes or longer before sampling commenced.

The effectiveness of fuel additives was determined by measuring CO_2, SO_2, NO_x and flame temperature. These measurements were compared at 30 minute intervals with and without additive treatment of fuel oil. This simple process of switching the fuel line back and forth from two fuel reservoirs prevented possible effects from burner instability and therefore permitted accurate quantitative assessment of any change as a result of the additive. NO was measured by chemiluminescence.

All additives tested under this study were either oil-soluble liquids or oil/benzene-soluble powders. The additives were selected on the basis of previous studies[2,3]. The maximum dosage of liquid additives was 1% and was reduced successively until no significant effect was observed. The liquid additives were used as supplied by the manufacturer. The actual metal content was determined by atomic absorption spectroscopy and ranged from 10-45 mmoles Mn per kg oil.

Results The decrease in the NO_x-emissions has been expressed in terms of an emission ratio, defined as: NO_x-emission in the presence of additives/NO_x-emission under baseline conditions. Plots of this ratio vs. the $(Mn)^{1/2}$ are linear (Figure 3). The results appear to be independent of the system used.

The difference in the slopes of the MnN- and MMTC-plots in Figure 3 suggests the operation of a ligand effect. The manganous acetylacetonate results (not plotted, since only two data points were obtained) would tend to support this conclusion. This observation makes any explanation of the effect based only on the metal highly speculative.

Flame temperature and NO-profiles were measured in order to obtain some insight into additive function. Examples of the isopleths that resulted are shown in Figures 4 and 5. (These data were obtained with the burner of Figure 2.) As indicated sampling was done at four levels above the origin of the flame and at nine points across the flame (in two directions). The isolines were drawn by linear interpolation of the actual measurements between any two sampling points. It would appear that the additive substantially decreases the rate of NO-formation.

A series of experiments were conducted by changing the oxygen index (vol % $O_2/O_2 + N_2$) in the presence of 1% manganese naphthenate (12.4 mmoles Mn/Kg oil). The data have been compared in Table 1. Of particular interest is the relative constancy of the NO_x-emission ratio (both as observed and as corrected to 12.7% CO_2) which indicates that although the NO-concentration in the stack gases increases over threefold when the index changes from 0.21 to 0.27, the percentage reduction effected by the additive remains about the same.

Discussion The nitric oxide levels presumably are controlled by the time-temperature history of the gases in the furnace[6,7]. The following sequence is usually considered for NO-formation

$$M + \tfrac{1}{2} O_2 \rightleftharpoons O + M$$

$$N_2 + O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N + NO \qquad 1)$$

$$N + O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} O + N_2 \qquad 2)$$

For a steady state concentration of N-atoms the rate of NO-formation is given by

$$\frac{d\,NO}{dt} = \frac{2\,k_1\,(O)\,(N_2)\left[1 - (NO)^2/K\,(N_2)\,(O_2)\right]}{1 + k_{-1}\,(NO)/k_2\,(O_2)}$$

If one assumes that step 1 is rate controlling and k_{-1} is small this expression simplifies to

$$\frac{d\,NO}{dt} = k_1\,(N_2)\,(O) = k_1\,K\,(N_2)\,(O_2)^{1/2}$$

where

$$K = \frac{(O)}{(O_2)^{1/2}}$$

One possible function of the additive may be competition for O-atoms in the post-flame zone via equation 3

$$\tfrac{1}{2}\,Mn + O \longrightarrow \tfrac{1}{2}MnO_2 \qquad 3)$$

Since the reduction in NO-concentration showed a square root dependence on the Mn-concentration, the rate equation may be modified as follows

$$\frac{d\,NO}{dt} = k_1 K (N_2)(O_2)^{\frac{1}{2}} - k_3 (Mn)^{\frac{1}{2}} (O)$$

$$= K (O_2)^{\frac{1}{2}} (k_1 (N_2) - k_3 (Mn)^{\frac{1}{2}}) \qquad 4)$$

which would predict that as $K (O_2)^{\frac{1}{2}}$ increases with increasing temperature - and assuming N_2 and $Mn^{\frac{1}{2}}$ to be constants - that the (k_1-k_3)-term controls the difference that is actually measured.

In the simplest case integration of 4 would yield

$$\left[(NO)_o - (NO)\right]_A = K (O_2)^{\frac{1}{2}} (k_1 (N_2) - k_3 (Mn)^{\frac{1}{2}})t$$

where $(NO)_o$ = NO-concentrations measured in the absence of additive, where (NO) = 0 = (Mn)

$\left[(NO)_o - (NO)\right]_A$ = NO-concentration measured in the presence of additive

t = residence time in the flame at a temperature where above mechanism would predominate

References

1. R. A. Beals, MASS-APCA Semi-Annual Technical Conference, Edison, New Jersey, May 12, 1972; p. 48.
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3. T. Shen and E. R. Altwicker, Paper presented at 4th Annual NOFI-meeting, Philadelphia, Pennsylvania, October 1971.
4. G. B. Martin, D. W. Pershing and E. E. Berkau, Effects of Fuel Additives on Air Pollutant Emissions from Distillate-Oil Fired Furnaces, OAP Publication #AP-87, June 1971.
5. H. Shaw, Transactions of the ASME, Journal of Engineering for Power, Paper #73-GT-S, pp. 1-8 (1973).
6. P. J. Marteney, Combustion Science and Technology 1, 461 (1970).
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8. E. R. Altwicker and T. Shen, Combustion Science and Technology (1974), in press.

FIGURE 1

Schematic Burner System

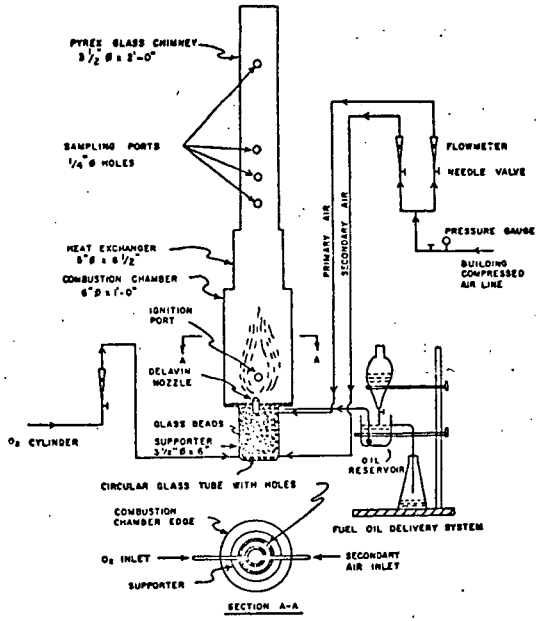


FIGURE 2

Experimental Burner

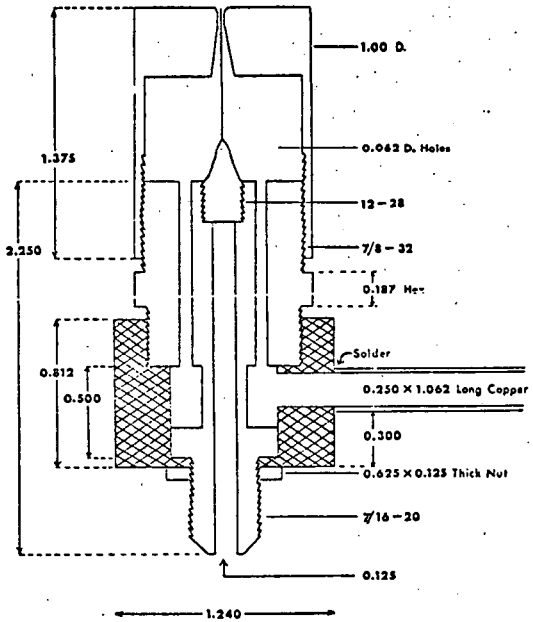


FIGURE 3

Reduction of Flue NO by Mn

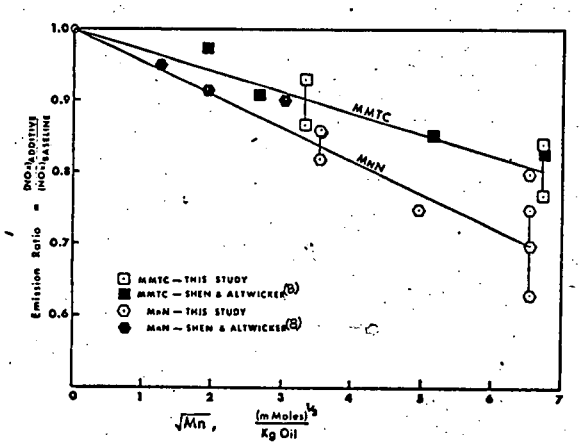


FIGURE 4

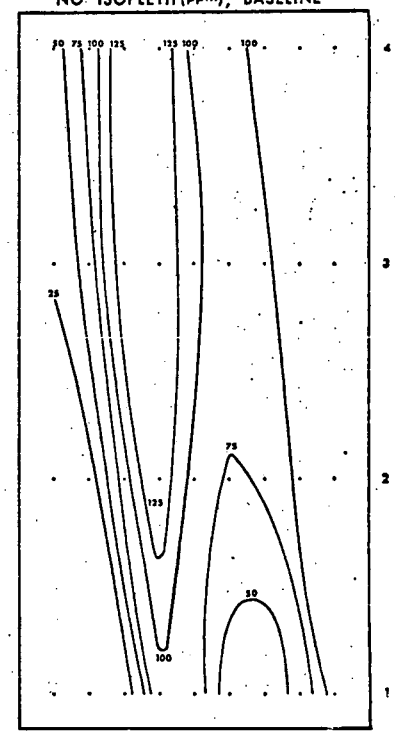


FIGURE 5

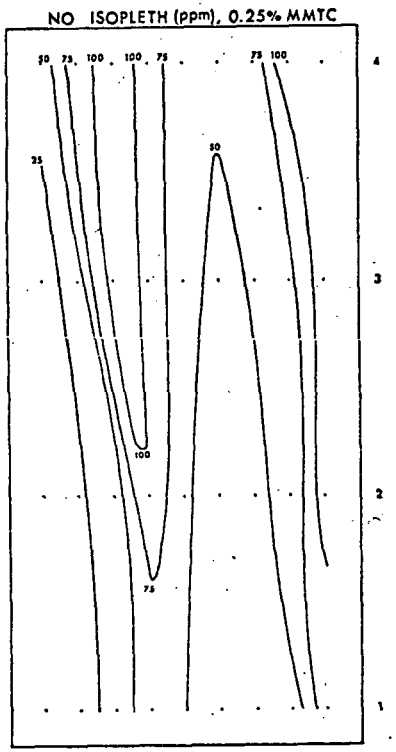


Table 1 - Effect of 1% Manganese Naphthenate at Varying Oxygen Indeces

Component	Oxygen Index			
	0.21	0.23	0.25	0.27
Baseline (no additive)				
NO_x, ppm	115 ± 7	180 ± 10	285 ± 20	450 ± 20
CO_2, %	12.7 ± 0.2	13.7 ± 0.2	14.2 ± 0.3	14.8 ± 0.3
Max. Flame Temp. °C	1280 ± 30	1410 ± 30	1490 ± 30	1540 ± 30
1% Manganese Naphthenate				
NO_x, ppm	96 ± 6	146 ± 10	236 ± 15	370 ± 20
CO_2, %	12.8 ± 0.2	13.9 ± 0.2	14.3 ± 0.3	14.8 ± 0.3
Max. Flame Temp. °C	1340 ± 30	1440 ± 30	1540 ± 30	1610 ± 30
NO_x-Emission Ratio	0.827	0.812	0.828	0.824
NO_x-Emission Ratio (corrected to 12.7% CO_2)	0.827	0.803	0.821	0.824
Flame Temp. Ratio	1.03	1.02	1.03	1.05

Figure 1

SCHEMATIC BURNER SYSTEM

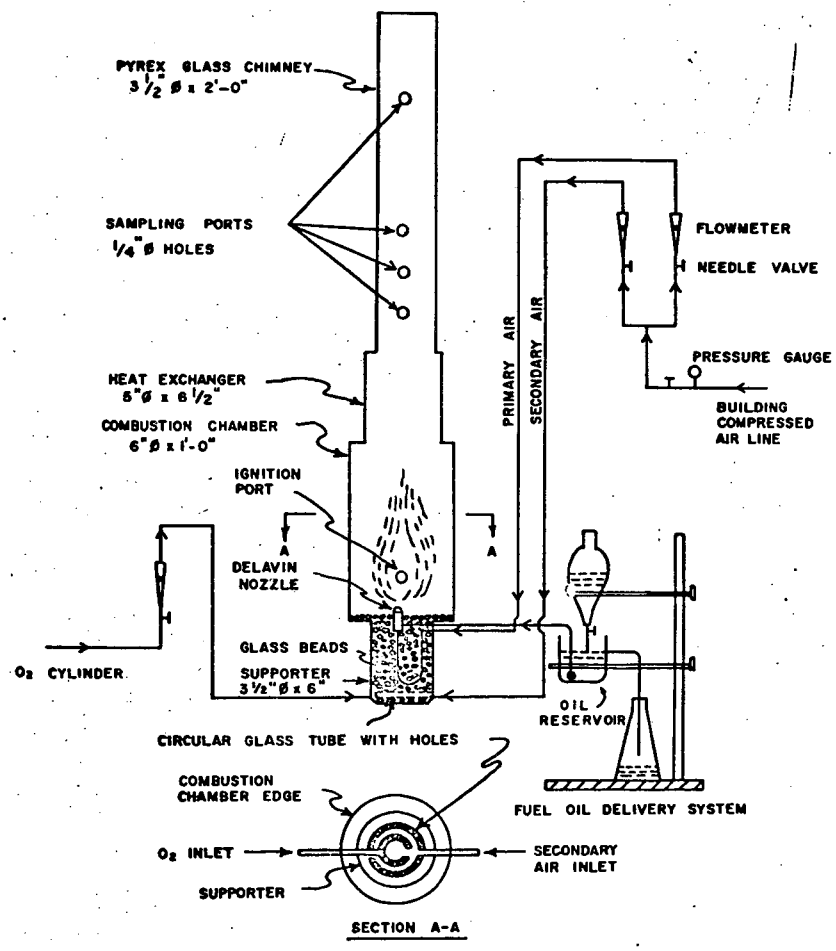


FIGURE 2
Experimental Burner

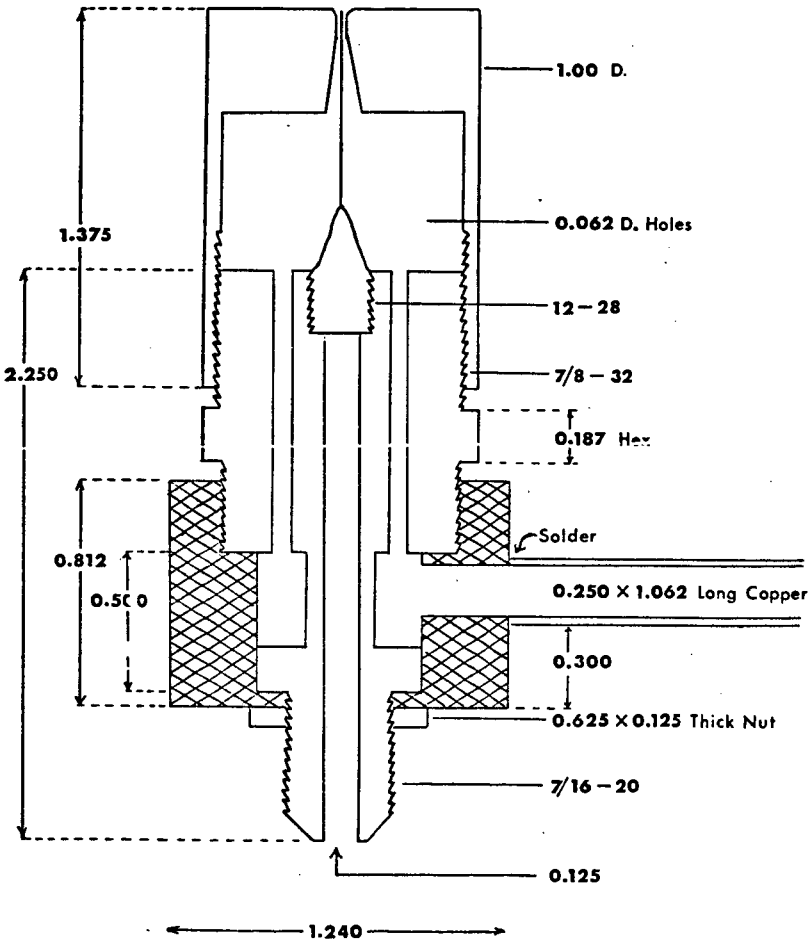


FIGURE 3
Reduction of Flue NO by Mn

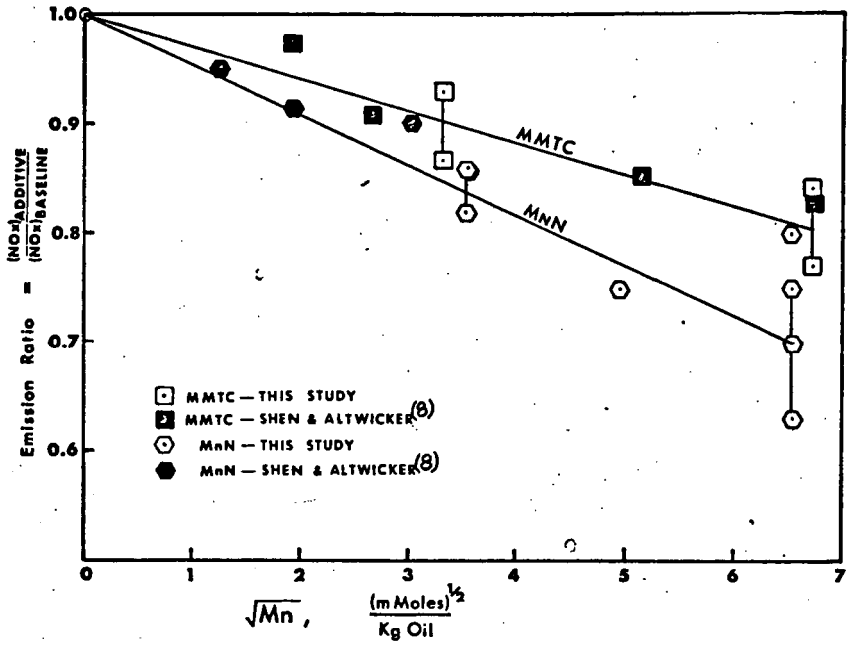


FIGURE 4

NO ISOPLETH (ppm), BASELINE

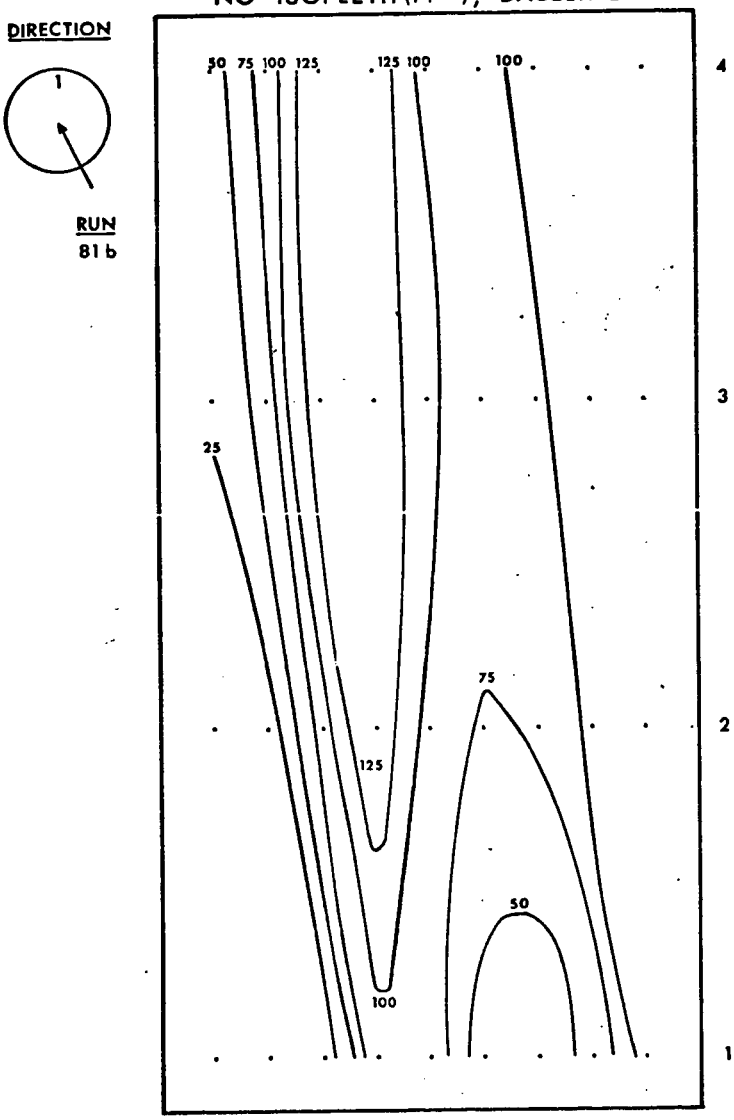
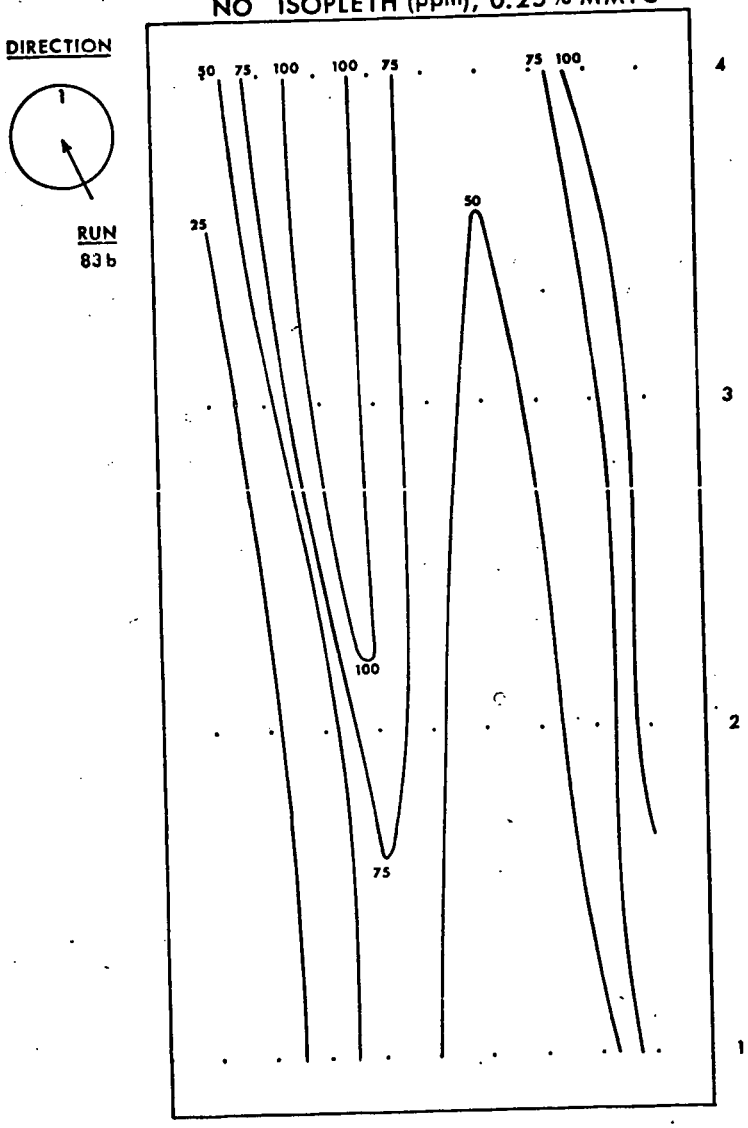


FIGURE 5

NO ISOPLETH (ppm), 0.25% MMTC



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