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## ENERGY & ENVIRONMENT DIVISION

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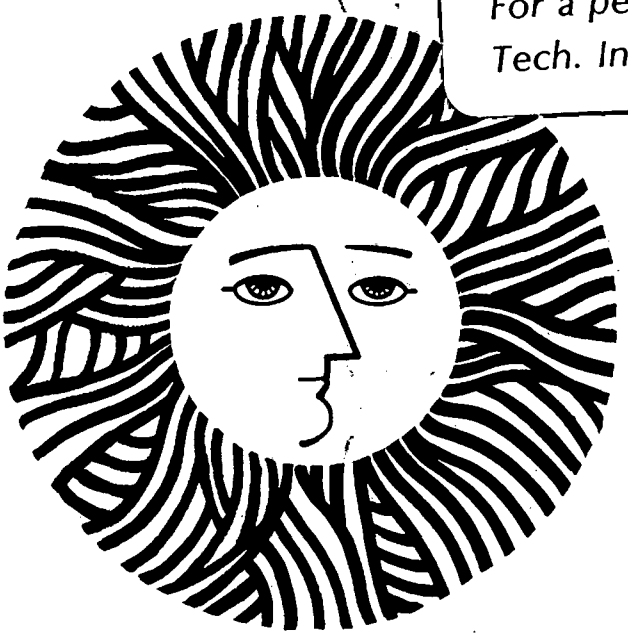

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# THE MEASUREMENT OF AMMONIA IN LEAN COMBUSTION EXHAUST GASES

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## ABSTRACT

Measurements of ammonia emissions in the exhaust gases of a lean-burning laboratory combustion tunnel were made using a variety of measurement techniques, using a common sampling method to allow meaningful inter-comparisons. Combustion parameters were varied from cold flow conditions to a range of equivalence ratios, sampling temperatures, and dopant concentrations. The advantages and disadvantages of the techniques are discussed with emphasis on their suitability for combustion research.

## INTRODUCTION

The measurement of ammonia in combustion exhaust gases is often difficult because of the high temperatures encountered when sampling, the large concentrations of water vapor and carbon dioxide, possible interferences by other combustion products, and the unusual chemical and physical properties of ammonia. Ammonia is often used in laboratory systems as a fuel and as a prototype fuel nitrogen compound (Song et al., 1981, Hahn and Wendt, 1981). It is also used as a reducing agent for nitric oxide in exhaust gases (Lyon, 1976). Since ammonia is an important chemical species in combustion, reliable and reproducible methods for measuring its concentration are required. It is also necessary to characterize these analytical methods for $NH_3$ to elucidate the limitations and interferences associated with each.

Various analytical methods have been employed to measure ammonia in combustion systems, including ion specific electrodes, gas chromatography, NO chemiluminescent analyzers, length-of-stain indicator tubes, infrared, microwave, and ultraviolet spectroscopy, and a host of wet chemical processes. We have examined some of these techniques in detail in an attempt to learn about potential interferences and limitations that might be encountered in quantifying ammonia in samples extracted from the product region of lean combustion mixtures, and to determine if any one technique can be considered most reliable and useful. We have limited ourselves to intrusive techniques that employ a common sample extraction technique, accomplished by probing with a quartz microprobe. Thus all of the techniques are identically biased, allowing for inter-comparison of the various analytical methods.

EXPERIMENTAL

The techniques used in this study vary widely in compexity and general acceptance. A brief description of the methods, with emphasis on the experimental details that are unique or non-standard in this study, is presented in the following section, and is followed by a critique of each method. The first method discussed, the sodium phenolate technique, will be used as as the "standard" for comparison, as this technique was found to be accurate and reproducible for a wide range of combustion conditions. Measurements of ammonia utilizing the different techniques were made under identical combustion and identical cold flow conditions to facilitate inter-comparison.

Measurements of $NH_3$ concentrations were made in an oil-fired laboratory combustion tunnel, details of which are published elsewhere (Lucas and Brown, 1982). Flow metering was accomplished with calibrated rotameters, and metered flows of reactants were used to calculate concentrations and equivalence ratios. The error in the measured flows is estimated to be $\pm$5%. The quartz sampling probes common to all of the methods were constructed from 3mm O.D., 2mm I.D. quartz tubing with the tip of the probes drawn to an orifice diameter of 0.3 to 0.5mm. The probes were located on the tunnel centerline well downstream of the visible flame front, and ~60cm downstream of the ammonia injection site. The temperature of the sampled gas varied from room temperature to ~1350K, with the equivalence ratio ranging from 0 to 0.95.

Sodium Phenolate Method

The sodium phenolate method of $NH_3$ analysis is a wet chemical colorimetric technique discussed by several investigators (Riley, 1944; Russel, 1944; Clear and Roth, 1955; Scheuer and Smith, 1955). In this

method ammonia is chlorinated to chloramine, $NH_2Cl$, and this is then reacted with sodium phenolate to form an indophenol dye of unknown structure which absorbs strongly at 632nm. In using this method we have developed a collection system that is useful for other measurement techniques, and it will be described in detail prior to the description of the chemical analysis.

Sample collection is accomplished by connecting the quartz sampling probe to two pyrex U-shaped collection tubes in series with unheated Teflon lines. The tubes are filled with 3mm pyrex spheres, and are coated with a dilute solution (0.005M) of phosphoric acid. The samples are pulled through the tubes at a rate of ~100 ml/min by a metal bellows pump which exhausts into a bubble flowmeter or a wet test meter. Two tubes are used to insure that the collection of the ammonia is complete. A schematic of the collection system is shown in Figure 1. A correction is made for the water in the exhaust gases that condenses in the sampling tubes. The concentration of water in the exhaust gas is measured gravimetrically using a magnesium perchlorate trap, and measuring the remainder of the gas with a flowmeter corrected for the vapor pressure of water. All reported $NH_3$ concentrations are corrected to the total exhaust volume.

Immediately after sampling the beads are transferred to 100ml graduated cylinders. The tubes and adapters are rinsed several times with distilled water, with all of the washings added to the sample. Additional water is added to dilute the sample to a convenient volume, typically about 60 ml. The total volume of the sample is recorded, and the following steps are performed on each sample: 10.0ml of the sample are pipeted into a test tube, and 1.0ml of saturated chlorine water($0^oC$) is added. The tube is stirred, and set aside for 5 minutes. Then 1.0ml of sodium phenolate

solution[1] and 1 drop of manganous chloride catalyst (0.003M) are added with stirring, and the solution set aside for at least twenty minutes. A blank is prepared in a similiar manner using the same water and reagents. A standard is also prepared using 0.200ml of an $NH_4Cl$ solution[2] and 9.8ml of water.

The optical density, O.D., of a sample and standard are measured against the blank at 632 nm, using a Beckman DU spectrophotometer with ~0.1mm slits and 1.0cm cells. The concentration of ammonia in the gas is then calculated from the following equation:

$$[NH_3]\ (ppm) = C\ \frac{(O.D.\ Sample)\ (Volume\ of\ liquid\ sample\ in\ liters)}{(O.D.\ Standard)(Volume\ of\ gas\ collected\ in\ liters)}$$

The solution concentrations used in this study were such that $C=2.0 \times 10^3$.

The optical density of the sample should be between 0.1 and 0.9 to remain on the linear portion of the calibration curve, as shown in Figure 2. For a 1.0 liter gas sample and a liquid volume of 60ml, concentrations of 35-315ppm can be measured. Different sample sizes can be used to extend the measurable concentration range.

The results using this method were, in general, quite good. Results obtained under cold-flow conditions are presented in Table I, and

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1. The solution is prepared by adding 7.2 g of sodium hydroxide to 300 ml of ammonia-free water. When cool 16.7 g of phenol is added, stirring until dissolved.

2. The standard solution is prepared by adding 55.0 mg of $NH_4Cl$ to 250 ml of ammonia-free water.

illustrate the accuracy and reproducibility possible with this method. Measurements made in hot combustion exhaust gases are more difficult to assess because of the reactions of $NH_3$ to form NO and reactions of $NH_3$ with combustion products, mainly the species involved in the reduction of NO via the Thermal $DeNO_x$ mechanism (Lyon, 1976). It was determined in low temperature exhaust and cold flow experiments that the normal combustion product interferences are negligible.

Interference by two other types of compounds was examined carefully in separate experiments. Possible interferences by higher amines were examined by preparing solutions containing these compounds. The dye formed from methyl amine exhibits an extinction coefficient of about 1/4 of that of ammonia. Dimethyl amine yielded no interference. The presence of sulfur species in the exhaust gases presents difficulties in that ammonia-sulfur species can readily form in the sampling train. These compounds are solid sulfates and bisulfates, formed from the reaction of $SO_2$ and $SO_3$ with ammonia and water, which decompose in the temperature range of 390 to 510K. There are two reasons for measurement errors caused by the presence of sulfur species: condensation of the ammonia prior to analysis, and direct interferences in the analytical process. The first problem is overcome by heating the sample lines and manifold to prevent formation of the solids, and by immersing the collection tubes in an ice-water bath to insure complete collection of the ammonia. The interference of sulfur compounds in the sodium phenolate analysis was checked by adding various sulfate, bisulfate and sulfite salts to known concentration mixtures of ammonia in water. In every case the interference caused by the sulfur was less than the uncertainty in the measurement itself, even at concentrations of the sulfur species that correspond to ~400 ppm in the combustion exhaust.

The disadvantages of the sodium phenolate method are the time required to perform an analysis, the batch nature of the sampling, and the somewhat large uncertainty ($\pm$ 10%) in the measurement for high ammonia concentrations (in the range of hundreds of parts per million). Cleaning of the requisite glassware is also tedious, since ammonia from a prior analysis was difficult to remove completely with simple washing procedures.

Chemiluminescent Method

The chemiluminescent method utilizes a hot catalytic surface to convert $NH_3$ in the presence of $O_2$ to NO, which is then detected by monitoring the emission from $NO_2^*$ formed from a reaction between NO and $O_3$. A Thermo Electron Corporation Model 12 NO chemiluminescent analyzer, CLA, is used to measure $NH_3$ concentrations in the $NO_x$ mode of the analyzer.

Because of the high water concentration present in the combustion products, the analyzer was modified to prevent water condensation. This is important since water condensation would result in a significant error in the ammonia measurement owing to the high solubility of ammonia in water. The capillary system used to regulate the flow to the reaction chamber was removed from the analyzer housing, and installed in a heated box adjacent to the sampling probe. A 15 cm long heated Teflon line was used to connect the quartz sampling probe to the capillaries. The sampled gas is thus held at a temperature sufficiently high (>330K) to avoid condensation until the pressure is reduced to near that of the reaction chamber (~10 torr), where condensation is no longer possible. The calibration gases for the analyzer are passed through the same heated network.

The efficiency of the stainless steel converter was measured as a function of the converter temperature and $NH_3$ concentration under cold flow

conditions. Figure 3 shows that the conversion efficiency increases with increasing converter temperature. In practice, the highest indicated temperature is used for all measurements (~1200K). At this temperature, results presented in Figure 4 show that the conversion efficiency is only a weak function of $NH_3$ concentration. Conversion rates were measured to be 93 $\pm$2 % for concentrations in the range from 250 to 1000 ppm.

The measurement of ammonia by the chemiluminescent technique is probably the easiest and most precise method to use for combustion applications. Sampling is accomplished on a continuous basis, with response times typically on the order of a few seconds. The instrumentation is quite rugged (suitable for field use), and requires no special chemical skills. However, care must be used when utilizing this method, for there are several potential problems that can negate the advantages of this method.

Precise analytical work requires that the instrument be calibrated in a variety of ways. A reliable NO calibration standard is needed. The calibration mixtures should be stored in stainless steel or aluminium cylinders, since it was found that NO would react slowly with conventional steel cylinders. The converter efficency must be determined as a function of temperature and ammonia concentration. The quenching of excited $NO_2$ in the analyzer should also be accounted for, particularly when high concentrations of water and hydrocarbons are present (Cuellar and Brown, 1982). The most important interference is the co-existence of other nitrogenous species which can be converted to NO in the analyzer. Species such as $NO_2$, HCN, and amines are of this type and can be converted to NO under the conditions normally used for $NH_3$ detection (Matthews et al., 1977). The interference of $NO_2$ can be eliminated by choosing another converter (Zolner, 1972). Performing a separate, independent measurement

of $NH_3$ using a technique that is not sensitive to these other nitrogenous compounds, such as the sodium phenolate technique described previously, is required to determine the presence or absence of these compounds. If they are present, the converter/CLA method is not useful for $NH_3$ measurements. A comparison of the chemiluminescent method and the sodium phenolate method is presented in Table II for both cold and hot flow conditions. The measurements made under cold flow conditions are compared with the calculated values, which are expected to be accurate for these conditions. Under combustion conditions, the agreement between the two methods is within experimental error of the measurements. It should be noted that little or no reaction of $NH_3$ and NO occurs in the catalytic converter of the chemiluminescent analyzer, even though the temperature of the converter is in the range employed in the Thermal $DeNO_x$ process, where NO is reduced to $N_2$ by the addition of $NH_3$. This is attributable to the low pressure in the converter (< 20 torr), which reduces the number of collisions.

The effect of fuel sulfur on the measurement of ammonia was assessed in a series of experiments in which thiophene was added to the fuel oil supply. At fuel sulfur concentrations in excess of 0.33%, the formation of ammonia-sulfur compounds was observed. These compounds tended to condense in the analytical train. This condensation could be eliminated if the entire analytical train and analyzer sections that are in contact with the sampled gases are heated above 500K. Poisoning of the converter by sulfur species was not observed at fuel sulfur concentrations below 0.63% by weight, as no permanent effect on the $NH_3$ conversion efficiency was noted.

Specific Ion Electrodes

The collection system developed for the phenolate method was also used to measure ammonia with a specific ion electrode. After collection of the

sample, the solution was transferred to a beaker of appropriate size and diluted with a known amount of ammonia-free deionized water. Ammonia concentrations were measured with a specific ion electrode (Orion Model 95-10), using both the direct calibration and known addition methods. The specific ion electrode allows ammonia vapor to pass through a permeable membrane, where it reacts with an internal ammonium solution which produces a change in the electrode potential. Any change in the sample which affects the partial pressure of ammonia in equilibrium with it results in a change in the electrode reading.

Experiments using air/ammonia mixtures show that the ammonia can be collected quantitatively, using our collection method or commonly used methods such as bubbling the gas through a dilute acid solution. It is important to note that dissolved $CO_2$ and other combustion products in the collection solution can result in errors in the electrode potential as high as 20%. The error is attributable to two factors: the $CO_2$ hydrolyzes to a weak acid and alters the pH of the solution, and also affects a change in the ionic strength of the solution which is dependent upon the total number of ionic species in solution. This change results in a different partial vapor pressure for ammonia, and hence a different electrode potential. The concentration of dissolved $CO_2$ can be reduced by minimizing the collection solution volume (prior to dilution to an appropriate volume for analysis), or by removing the $CO_2$. It was found that five minutes of vigorous mechanical stirring was sufficient to remove the $CO_2$ from a saturated solution at room temperature. It is more difficult to assess the ionic strength of a combustion condensate solution. To alleviate the ionic strength problem, one should use the known addition method for determining $NH_3$ concentrations. The direct calibration method, although somewhat

simpler for a large number of samples, should not be used for combustion samples. When errors attributable to changes in pH and ionic strength are accounted for, the ion electrode method compares favorably with the sodium phenolate method. The two methods agree to within 10%, the estimated uncertainty in the measurements for samples extracted from lean combustion exhausts.

The disadvantages of the use of specific ion electrodes for $NH_3$ measurements are those associated with any wet chemical technique; batch sampling, long analysis time, and the need for reasonable laboratory analytical skills by the operator. The method also suffers from a large amine interference, though this is not a problem in most lean combustion mixtures. This method can be used in place of the sodium phenolate technique as a check on the chemiluminescent measurements.

Length-Of-Stain Indicator Tubes

Indicator tubes are frequently used in field studies to confirm the presence of certain compounds. Ammonia indicator tubes respond to a neutralization reaction: as ammonia is drawn into the tube a reaction occurs with phosphoric acid, this neutralization reaction is monitored by an indicating pH reagent which changes color from pink to yellow. Indicator tubes of the Kitagawa type (Matheson) were used in two different modes. The first method connected the tube to the sampling probe with a short (5 cm) piece of Teflon tubing, while the second method placed the tube in direct contact with the probe. In both cases the volume of sample pulled through the tube was that recommended by the manufacturer.

Indicator tubes were found to perform reasonably well, considering the simplicity of the technique. The technique requires few laboratory skills, and the results are evident immediately after the end of the sampling

procedure. The major disadvantages for research work are the lack of resolution, long sampling times, and the use- and-throw-away nature of the tubes. Typically, for ammonia concentrations in the range of hundreds of parts per million, the tubes had a resolution of about 20 ppm. The tubes cannot be used for continuous monitoring, and sampling time is on the order of minutes. Interferences from combustion products were not characterized by direct measurements; however, the manufacturer states that the presence of compounds such as CO, $CO_2$, and low concentrations of water (< 7%) do not affect the accuracy, but the presence of $SO_2$ at 50ppm results in lower readings.

## CONCLUSIONS

We have discussed several techniques commonly used for measuring ammonia in lean combustion systems. We summarize our findings in Table III by listing the resolution, sensing limit, accuracy, analysis time, interferences, and a qualitative assignment of the ease of analysis using the sodium phenolate, $NO_x$ CLA, specific ion electrode, length-of-stain tube, and GC methods for measuring ammonia. Because of the difficulties and interferences that plague these techniques, we suggest that it is necessary to use more than one method to insure the accuracy which is required in most research studies.

## ACKNOWLEGEMENTS

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TABLE I

Cold Flow $NH_3$ Mesurements (ppm)

| Calculated | Measured with Phenolate Method |
|---|---|
| 0 | 4.5 |
| | 0.1 |
| | 0.3 |
| | 8.0 |
| | 3.9 |
| 43 | 37 |
| | 38 |
| 807 | 755 |
| | 821 |
| 1000 | 1024 |
| | 1057 |
| | 1053 |

Table II

Ammonia Measurements in Combustion Exhaust

| T (K) | $\phi$ | [NO] (ppm) | $[NH_3]$ (ppm) | |
|---|---|---|---|---|
| | | | $NO_x$ CLA Method | Phenolate Method |
| 1100 | 0.83 | 320 | 677 | 653 |
| 1169 | 0.95 | 117 | 318 | 352 |
| 1229 | 0.78 | 29 | 340 | 362 |
| 1233 | 0.74 | 265 | 27 | 32 |
| | | 31 | 249 | 274 |
| 1235 | 0.73 | 350 | 8 | 12 |
| | | 49 | 2 | 1 |
| 300 | 0 | 0 | 810 | 788 |

TABLE III
Summary of Ammonia Measurement Techniques

| METHOD | RESOLUTION (ppm) | SENSING LIMIT (ppm) | ACCURACY AT 100 PPM | ANALYSIS TIME | MAJOR INTERFERENCES | EASE OF ANALYSIS |
|---|---|---|---|---|---|---|
| Sodium Phenolate | 1 | 5 | 10% | 30 min | methylamine | - |
| $NO_x$ CLA | 1 | 5 | 5% | 15 sec | oxidizable nitrogen cmpds, third body quenching | ++ |
| Specific Ion Electrodes | 1 | 1 | 10% | 10 min | $CO_2$, dissolved species | - |
| Length-of-stain Tube | 20 | 1 | 20% | 3 min | $SO_2$ | ++ |
| GC[1] | 10 | 50 | 10% | 15 min | Water | + |

1. TC detector, $0.5cm^3$ sampling loop, Poropak type packing(Banna and Branch, 1978).

## FIGURE CAPTIONS

1. Ammonia collection apparatus used for the sodium phenolate and specific ion electrode methods.

2. Calibration curve for the sodium phenolate method: optical density of dye as a function of initial $NH_3$ amount.

3. Conversion of $NH_3$ to NO as a function of indicated converter temperature at an ammonia concentration of 1000 ppm in air.

4. Conversion of $NH_3$ to NO as a function of $NH_3$ concentration at a constant converter temperature.

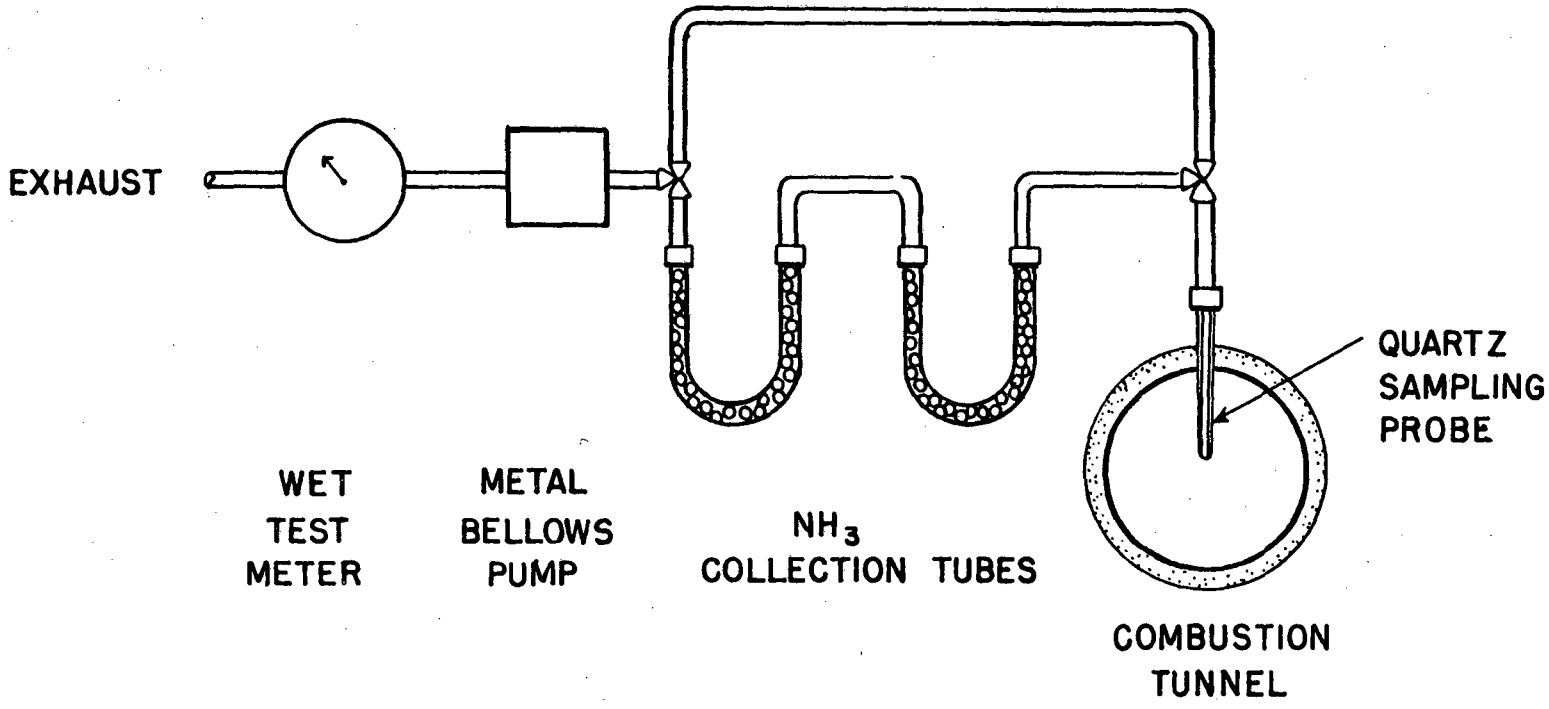


Figure 1

XBL 812-8276

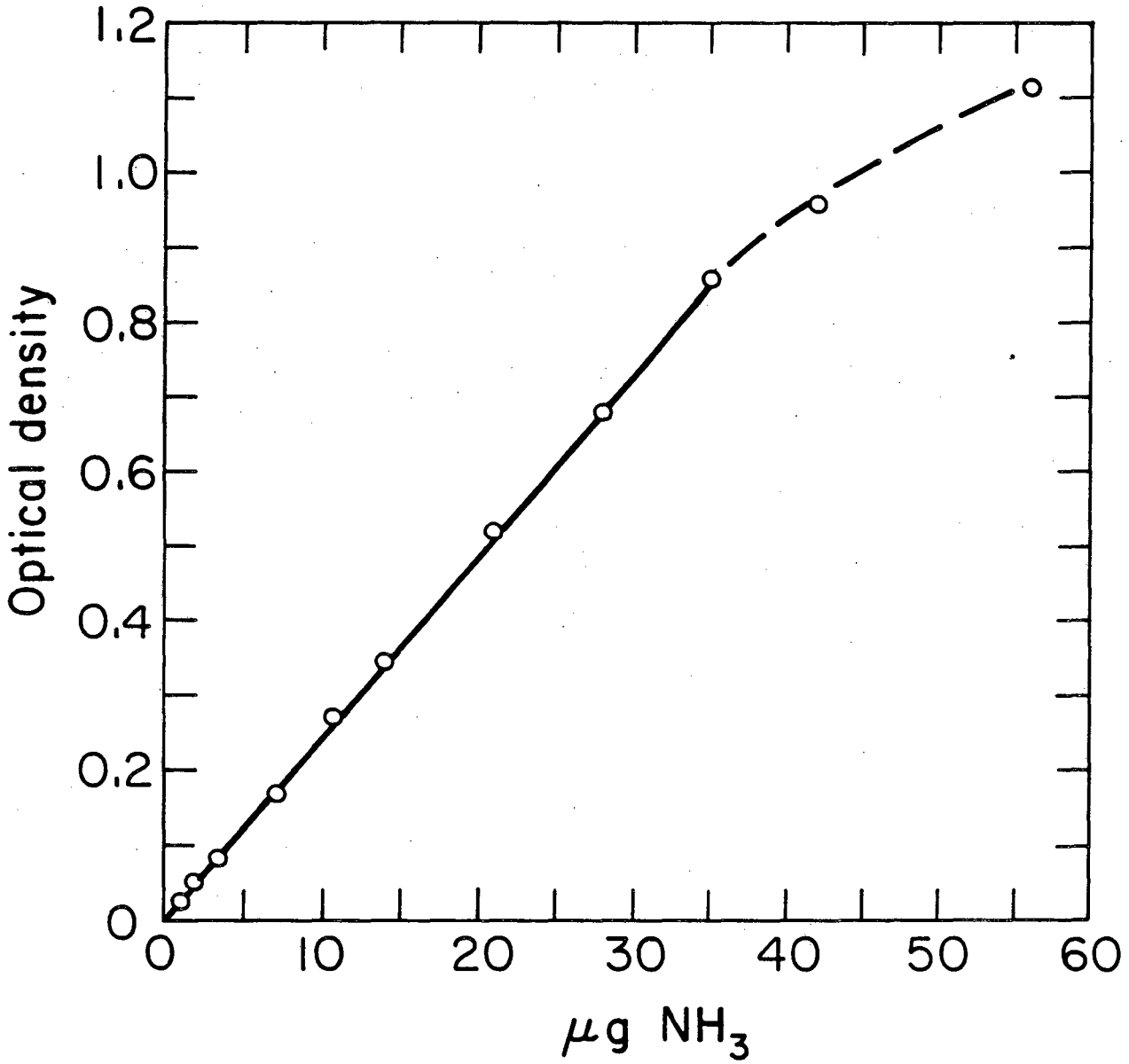


Figure 2

XBL 803-181

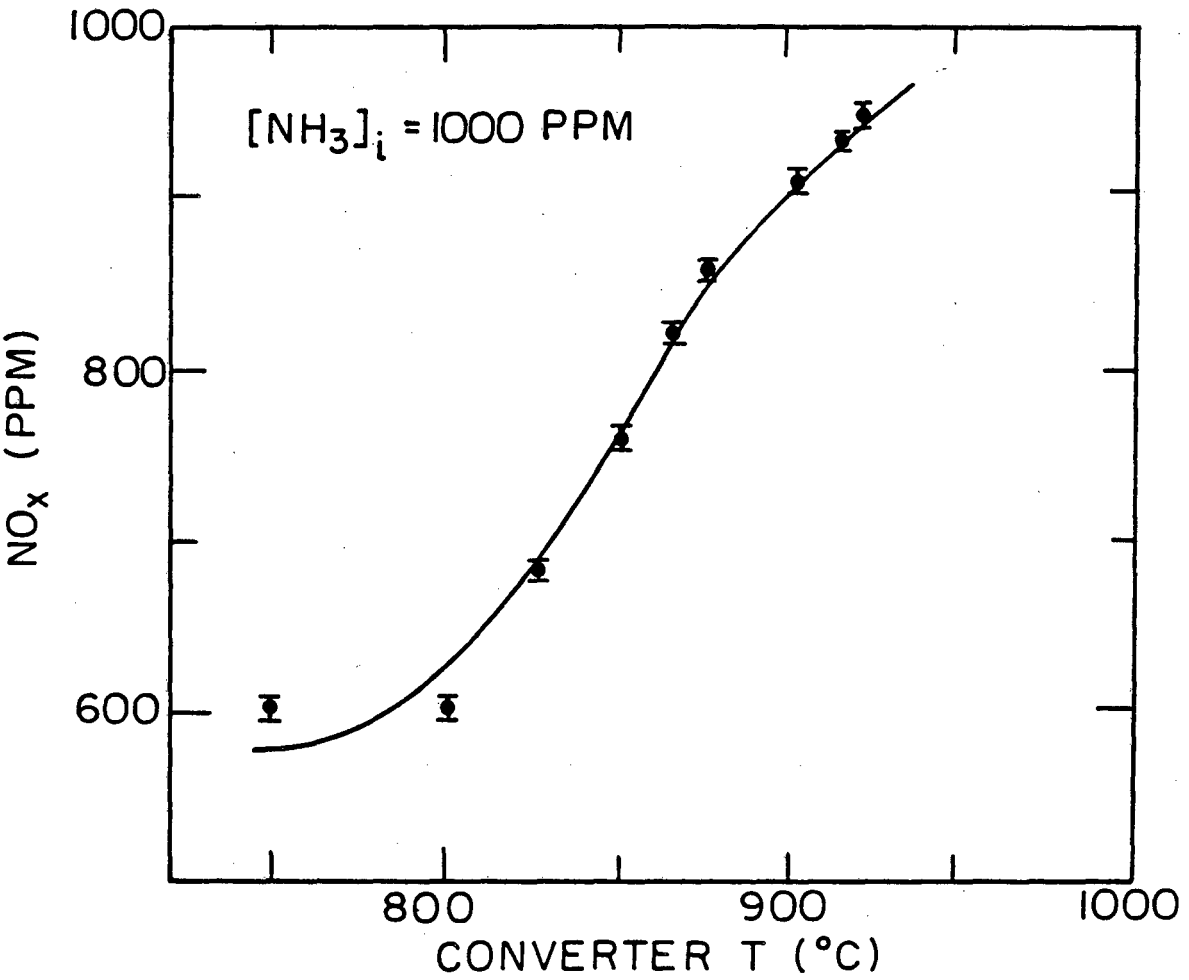


Figure 3

XBL 8012-13386

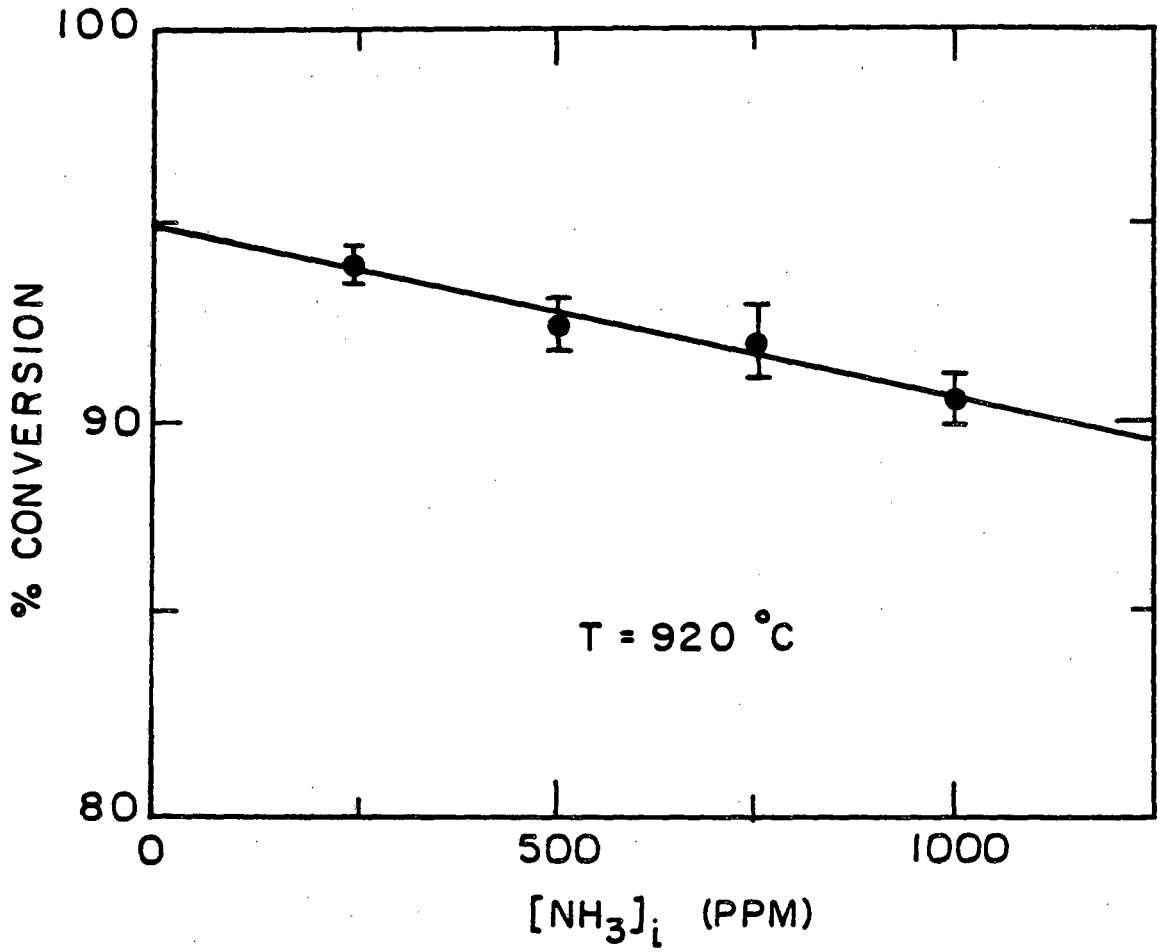


Figure 4

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