



A Fluorometric Method For Ammonia Analysis in Ambient Air

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Introduction

- Although existing sampling and analytical methods for ammonia may be adequate for evaluating exposure relative to the OSHA-PEL (50 ppm TWA), many projects involving the short-term measurement of ppb concentrations require more sensitive methods.
- This project focuses on the modification of a fluorometric method previously developed for analysis of ammonium in marine and freshwater samples¹ to enable measurement of low concentrations of ammonia in ambient air.
- The modified approach combines the sorbent-tube collection techniques of current methods^{2,3} for ammonia sampling with analysis using a digital filter fluorometer.

Experimental Design and Methods

- The research design consisted of three phases:

Phase I

- Two experimental protocols from the published fluorometric method for ammonium samples were reproduced in the laboratory using liquid standards, i.e., deionized (DI) water spiked with ammonium stock solution.

Protocol A

Sample desorbed with 80 mL D.I.
20 mL of working reagent (OPA) added
2 Hr room temperature incubation

Protocol B

Sample desorbed with 10 mL D.I.
2.5 mL aliquot transferred to 20 mL scintillation vial
10 mL of working reagent (OPA) added
2 Hr room temperature incubation

Sample transferred to 4.5 mL cuvette and analyzed using a digital filter fluorometer with an excitation wavelength of 365 nm and an emission wavelength of 420 nm.

- Once the analytical method was established, a collection protocol employing an acid-treated solid adsorbent was evaluated.
- A two-factor experimental design was used to evaluate the effects of 1) sorbent tube manufacturer and sorbent mass, and 2) experimental protocol on Limit of Quantification (LOQ) for tubes spiked with DI water containing known quantities of ammonium.

Phase II

- Performance of the new method was evaluated by examining limit of detection (LOD), limit of quantification (LOQ), linearity, analyte recovery from the sample medium, and stability on the sample medium.

Phase III

- Low concentrations of ammonia were generated in a dynamic test-atmosphere chamber.
- Samples were collected and analyzed and experimental results were compared to predicted concentrations based on the known dilution air and test-gas flow rates.

Results and Discussion

Phase I

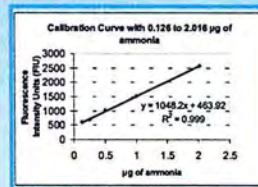


Figure 1: Calibration curve from spiked samples.

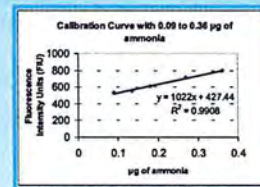


Figure 2: Calibration curve for reduced range.

- Preliminary Protocol A calibration curves for two different concentration ranges are presented in Figures 1 and 2. Responses were linear over the concentration ranges examined.
- Limits of detection (LOD) and quantification (LOQ) were defined as 3 and 10 times the standard deviation of blank samples, respectively.
- ANOVA results (Figs 3,4) indicate that LOQ is minimized using Supelco sorbent tubes, 75 mg of sorbent, and Protocol A.

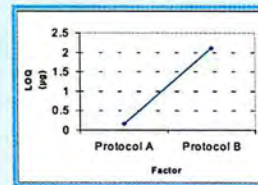


Figure 3: Main Effects Plot for LOQ.

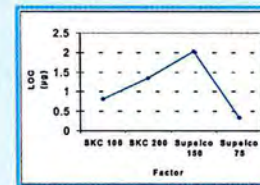


Figure 4: Main Effects Plot for LOQ.

Phase II

Table 1: Analyte Recovery Results

Amount of Ammonia (µg)	% Recovery at Day 1	% Recovery at Day 7
0.252	102.5	96.4
0.504	100.3	99.6
1.008	97.5	98.7
Ave	100.1	98.23
SD	2.51	1.65

- When stored at room temperature for one and seven days, spiked samples had a mean percent recovery of 100.1 ± 2.51 and 98.23 ± 1.65 respectively for three levels of fortification.

Phase III

- Concentrations determined experimentally for sample collection times of eight and fifteen minutes at flow rates of 200 mL/min, 100 mL/min and 50 mL/min were within +/- 20% of known chamber concentrations.

Table 2: Results from the test chamber

Ammonia Concentration (ppm) ¹	Sample Time (min)	Sample Flow Rate (mL / min)	Predicted Sample Mass ² (µg)	Experimental Sample Mass (µg)	% Difference ³
4.00	8	102	2.28	2.72	19.2
	8	101	2.27	2.61	14.9
	8	101	2.28	2.61	14.5
1.00	8	101	2.26	2.55	12.8
	15	201	2.10	2.05	-2.5
	15	101	1.06	1.00	-5.6
0.500	15	50.6	0.530	0.546	3.0
	15	201	1.06	1.03	-2.7
	15	99.9	0.524	0.511	-2.5
0.250	15	50.7	0.266	0.215	-19.2
	15	201	0.530	0.493	-6.9
	15	101	0.265	0.261	-1.5
0.126	15	50.8	0.134	0.131	-2.2
	15	201	0.265	0.264	-0.4
	15	103	0.136	0.165	21.3
	15	50.8	0.067	0.113	68.6

¹Calculated from Dilution air and test gas (404.3 ppm) flow rates.

²Calculated from chamber concentration, sample time and sample flow rate.

³% difference = $\frac{\text{Experimental Mass} - \text{Predicted Mass}}{\text{Predicted Mass}} \times 100\%$

*Predicted Sample Mass lower than LOQ of 0.084 µg

Conclusions

- The LOQ obtained by this method (0.08 µg) represents a 20-300 fold decrease compared to existing methods (LOQ = 1.7 and 25 µg, for NIOSH 6015 and OSHA ID-188, respectively).
- This modified approach offers an accurate and significantly more sensitive method of sampling and analysis for the characterization of trace concentrations of ammonia.

Acknowledgments

Support for this project is gratefully acknowledged:

- The National Institute for Occupational Safety and Health, SERCA 5K01 OH00177-04
- Wilson Research Initiation Grant Program, College of Earth and Mineral Sciences, Penn State University

References

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- 2National Institute for Occupational Safety and Health. NIOSH, ed. Ammonia by IC - Method #6016. In NIOSH Manual of Analytical Methods. Fourth ed. Cincinnati, OH, NIOSH. 1996.
- 3Occupational Safety and Health Administration. (1991) Ammonia in workplace atmospheres - solid sorbent: Method ID-188. OSHA Analytical Methods Manual (2nd ed).