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OPTIMIZATION OF THE TUNGSTEN OXIDE TECHNIQUE FOR MEASUREMENT OF ATMOSPHERIC AMMONIA

By

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INTRODUCTION

Hollow tubes coated with Tungstic Acid have been shown to be of value in the determination of ammonia and nitric acid in ambient air[1]. Practical application of this technique was demonstrated by Lebel[2] utilizing an automated sampling system for in-flight collection and analysis of atmospheric samples. Due to time constraints these previous measurements were performed upon tubes that had not been well characterized in the laboratory. As a result the experimental precision could not be accurately estimated. Since the technique was being compared to other techniques for measuring these compounds, it became necessary to perform laboratory tests which would establish the reliability of the technique. This report is a summary of these laboratory experiments as they are applied to the determination of ambient NH_3 concentration.

The first part of the report is a straightforward repeatability study to assess whether tubes could be prepared in such a way that they would give (1) similar results upon repeated sampling, and (2) different tubes would yield the same result when applied in the analysis of a known sample. The second part of the report will be concerned with evaluating how much time can elapse before an exposed tube has to be analyzed. The third part of the report will summarize a study to determine the "shelf life" of the tubes, i.e., how long will a given tube maintain its efficiency for NH_3 collection and whether or not environmental contamination can occur either by leakage,

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[1] Braman, R.S., Shelley, T.J. and McClenny, W.A., Anal. Chem. 54, 358-364 (1982).

[2] P. Lebel, personal communication.

or by outgassing of the tube walls. The last part of this report establishes calibration procedures for the tubes in order that they may be used in field studies.

REPEATABILITY STUDY

The repeatability study involved ten tubes prepared according to the procedures outlined in Ref. 1. The experimental procedure was the same for each tube. Each tube was preconcentrated by drawing a one L/min. sample from a manifold for a five minute time span at a NH_3 concentration of 7.11 ng/L (10.21/ppb). Total dilution flow was maintained at 6.4 L/min. The tube was then manually removed from the sampling manifold and attached to the analysis system by means of teflon fittings. The tube was then heated in excess of 350°C with a heating coil for five minutes while under a He flow. The desorbed NH_3 then passed over a hot gold catalyst (heated to over 600°C) which converted the NH_3 to NO. The NO was detected by the chemiluminescent detection system. Each tube was allowed to cool ten minutes after heating before another analysis was performed. The areas of the observed peaks were determined by measuring both peak height and width for a given peak on the chemiluminescence detector.

The data for all ten tubes is summarized in Table I. The areas range from 1.68 to 1.83 for the ten tubes, a variability of slightly less than 10%. Such variability is quite small given the crudeness in the area determination. These numbers are most likely maximum estimates of the error in the technique. The variability will be significantly smaller on the automated system when the signal is digitized and electronically integrated.

Table I: Summary of the repeatability studies.

Tube Number	Number of Trials	Average Peak Area (cm^2)	Standard Deviation
147	56	1.68	.15
146	64	1.77	.22
145	45	1.70	.18
144	55	1.83	.22
143	39	1.69	.15
141	9	1.70	.09
140	19	1.76	.16
138	22	1.72	.13
129	13	1.73	.19
126	9	1.77	.07

Total number of trials = 331

Overall average = 1.74

Overall standard deviation = .18

Percent variance = 10%.

STABILITY OF EXPOSED TUBES

The stability of the exposed tubes was determined using the same overall treatment and analysis procedure, as in the previous section, with the exception that after exposure to NH_3 the tubes were capped with glass plugs and teflon tubing connectors. The loaded tubes were then shelved at room temperature and analyzed at designated time periods. The results are summarized in Table II. Fairly consistent results were obtained for the first thirty hours of storage. However, storage of the tubes for a period of time longer than thirty hours is not recommended. There was a marked increase in the average value after this period of time with more than a doubling of the standard deviation. The best data were obtained when the tube was held for less than ten hours. For this period of time, the percent of uncertainty was less than 10%, whereas, for greater than 10 hours, the percent of uncertainty became greater than 30%. It is apparent that the eventual experimental protocol requires as rapid an analysis of an exposed tube as possible, preferably within the first ten hours after exposure.

TUBE BLANKS

The effect of shelf time on a previously exposed tube also needed to be determined. The experimental procedure was the same as before. At the end of the analysis the tube was capped and stored for a set period of time prior to the next exposure. The tube was then exposed to a given flow and then analyzed as before. The data are summarized in Table III.

The data is conveniently divided in two groups, one group was analyzed for the second time on the same day and the other when the tubes were held overnight. It is readily apparent that the scatter of the data is much worse at longer hold times with the scatter becoming significant after a

Table II: Summary of data for tube stability after sample exposure.

Holdtime after Exposure (hrs)	Number of Trials	Average Area in cm^2	Standard Deviation
0-10	14	1.65	.12
11-20	16	1.62	.22
21-30	17	1.65	.21
31-60	14	1.84	.62
61-90	26	1.75	.43
91 & above	27	2.00	.50

Total number of samples = 114

Overall average = 1.77

Overall standard deviation = .43

Table III: Summary of blank tube storage lines. All numbers are peak areas.

Hold time (hrs)	1	2	3	4	5	6	7
	1.89	1.94	1.82	1.55	1.99	1.86	1.49
	1.91	1.70	1.61	2.14	1.77	2.19	2.10
		1.80	1.86	1.73	1.76	2.07	
		1.56	1.41	1.93	1.76		
		1.70	1.41	1.58	1.69		
			1.73	1.48	1.42		
			1.51	1.54	1.87		
			2.00	1.96	1.69		
			1.80	1.97	1.86		
				1.70	1.53		

Hold time (hrs)	19	20	21	22	23	24	25
	1.68	1.97	1.98	1.26	1.68	1.41	1.96
	1.69		2.12	1.19	1.42	1.25	
	1.79		1.82	1.64	1.86		
			2.08	1.98			
			2.01	1.61			

Hold time (hrs)	26	27	28
	1.69	1.95	1.71
		1.53	

Summary:

Hold time =	1-7	19-30	1-30
Total samples =	41	29	70
Average =	1.76	1.64	1.71
Standard deviation =	.2	.41	.31

hold time of six hours. A hold of overnight results in a doubling of the standard deviation with a slight lowering of the average area determined. The data seems to be more self-consistent if the tubes are used quickly.

CALIBRATION OF THE TUBES

The calibration curve for the tubes must be established in order that the observed areas produced by the detector could be directly interpreted in terms of NH_3 concentration in ppb. The exposure of the column to NH_3 was varied by changing the NH_3 exposure time of the tube. Doing so yielded evenly spaced dosages of NH_3 in ng/L. The summary of the data is shown in Table IV. Since the first minute of flow was not steady and was actually 860cc and the actual flow was 1057 cc/min instead of 1000cc/min as given in Table IV the data had to be corrected. The corrected data is shown in Table V.

The resultant calibration curve is shown in Figure 1. The curve is reasonably linear with perhaps a slight curvature at the upper end, over this range of concentration. The equation for the line is: peak area = $.057\ [NH_3] + .055$ with a correlation coefficient of .96

Standard deviation for each point on the curve is a small fraction of the observed area becoming neglible at sufficiently high loads. At loads above 50 ng/L the overall uncertainty is less than 5% for the manual system.

These calibrations were performed for two different tubes with both tubes yielding a linear calibration curve with good reproducibility between runs. The results obtained with these tubes have at most a 15% variance at low concentrations and in general less than 8% at higher concentrations for the manual system. The automated, digitized system will certainly yield a reproductability with less than 2% scatter in the data.

Table IV: Calibration data for tube #4.

Mass of NH_3 (ng/L)	7	14	21	28	35	49	54
Area (cm^2)	.65	1.13	1.30	1.51	2.02	2.75	4.34
	.63	1.03	1.23	1.41	2.01	2.90	4.13
	.62	1.09	1.35	1.35	1.84	2.64	
	.84	1.01	1.59	1.54	1.62	2.89	
	.81	1.09	1.23	1.52	1.82	3.04	
	.70	.70	1.37	1.38	1.79		
	.64	.83	1.24	1.74			
	.64	.95	1.20	1.54			
	.65	.88	1.30	1.68			
	.60	.86	.98	1.55			
Average area	.68	.96	1.28	1.52	1.85	2.84	4.24
Std. Dev.	.08	.13	.15	.15	.14	.14	.10

Table V: Corrected data of table IV for the varying first minute of flow and the reconciliation of the flow meter.

Sample load (L)	Load (ng)	Load (pp6)	Peak area (cm^2)
.917	6.52	9.36	.68
1.974	14.04	20.16	.96
3.031	21.55	30.95	1.28
4.088	29.07	41.74	1.52
5.145	36.58	52.53	1.85
7.259	51.61	74.11	2.84
9.373	66.64	95.70	4.24

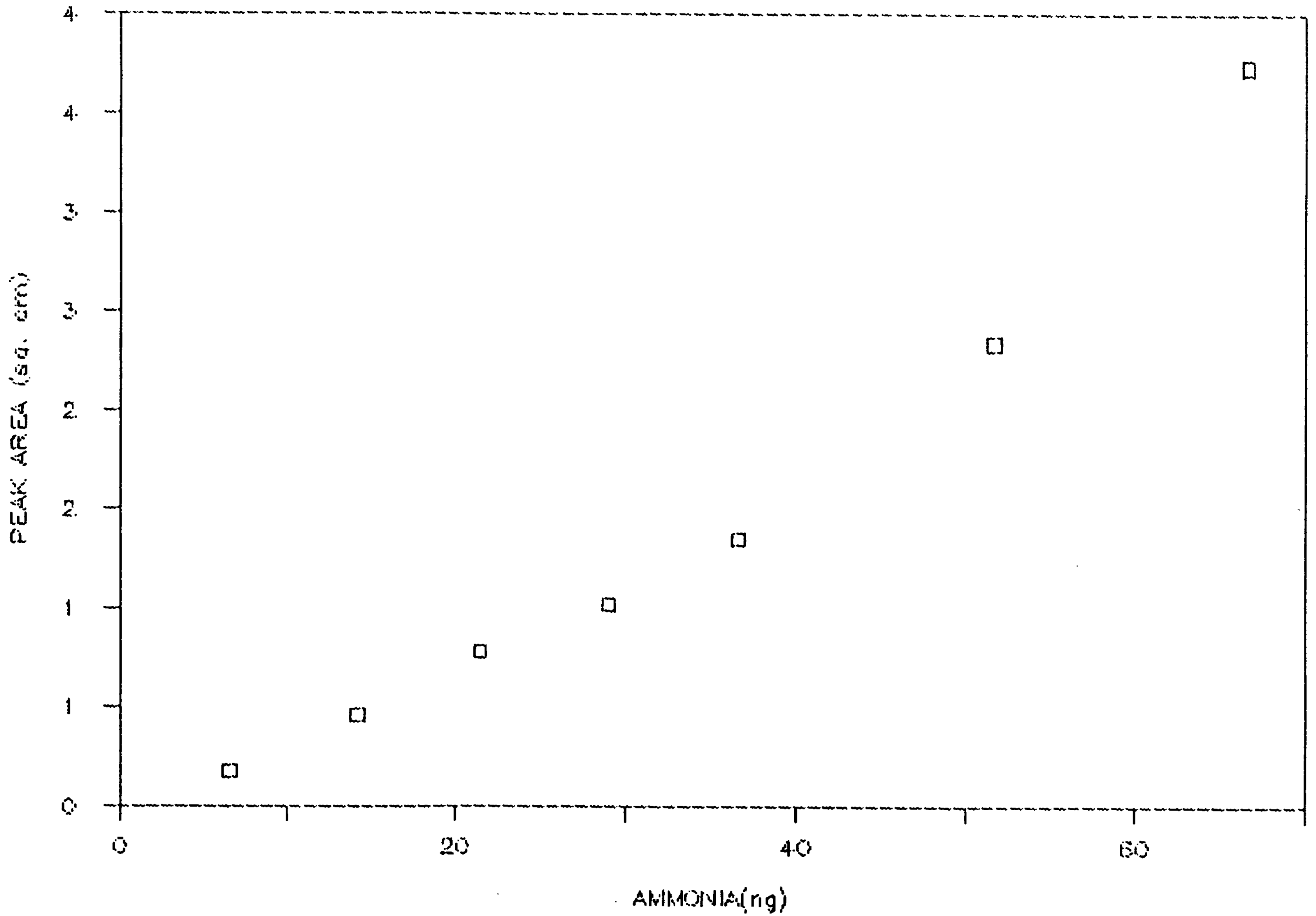

Figure 1