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Evaluation Test Report Agrico Chemical Company Blytheville, Arkansas

DEVELOPMENT OF ANALYTICAL PROCEDURES FOR THE DETERMINATION OF UREA FROM UREA MANUFACTURING FACILITIES

PROJECT NO. 79-NHF-13

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PREFACE

The work reported herein was performed by personnel from TRC Environmental Consultants, Inc. (TRC) and the U.S. Environmental Protection Agency (EPA). The scope of work, issued under EPA Contract No. 68-02-2820, Work Assignment Number 11 (and as part of Work Assignments 9, 19, and 20) was under the supervision of the TRC Project Manager, Mr. Willard A. Wade III. Mr. Eric A. Pearson of TRC was responsible for summarizing the test and analytical data presented in this report. Chemical analyses were performed at the TRC laboratory in Wethersfield, Connecticut under the direction of Ms. Joanne M. Marechese and Ms. Margaret M. Fox.

Mr. Gary D. McAlister, Office of Air Quality Planning and Standards, Emission Measurement Branch, EPA, served as Lead Chemical Engineer and was responsible for developing and evaluating the analytical procedures used in this report.

Mr. Clyde E. Riley, Office of Air Quality Planning and Standards, Emission Measurement Branch, EPA, served as Technical Manager and was responsible for coordinating this method evaluation program.

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July 31, 1980

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1.0 INTRODUCTION

1.1 Background

Section 111 of the Clean Air Act of 1970 charges the Administrator of the United States Environmental Protection Agency (EPA) with the responsibility of establishing Federal standards of performance for stationary sources which may significantly contribute to air pollution. When promulgated, these standards of performance for new stationary sources (SPNSS) are to reflect the degree of emission limitation achievable through application of the best demonstrated emission control technology. Emission data, collected from controlled sources in the particular industry of concern, provide a portion of the data base used by EPA to develop SPNSS.

In the development of SPNSS, EPA follows a policy of establishing reference sampling and analysis methods for each regulated source category and pollutant. Current emphasis on the control of urea particulate emissions has created a need for a urea analysis reference method.

This report presents the results of urea analytical method investigations conducted under EPA Contract #68-02-2820 as Work Assignment Number 11 and as part of Work Assignment Numbers 9, 19, and 20. These results will be used as a data base for the development of a urea analysis reference method.

1.2 Introduction to Urea and Ammonia Analysis Methods

Two urea analysis methods and three ammonia analysis methods have been used by EPA and its contractors during the emission testing programs conducted for the development of SPNSS for the urea manufacturing industry. Each of these analysis methods and their variations are briefly described in this section. The methods themselves are presented in their entirety in Appendices A and B.

1.2.1 Urea Analysis Method

P-dimethylaminobenzaldehyde (PDAB) Method

- Direct Method: The PDAB color reagent is added to the sample, and after color development has occurred the absorbance of this solution is measured with a blank-zeroed spectrophotometer. The measured absorbance is related to urea concentration through a calibration curve prepared from the absorbances of standard urea solutions.

- Preliminary Distillation Method: A buffering compound is added to the sample and this solution is then distilled (boiled) to remove ammonia and other potential interferences. The PDAB reagent is then added and the solution absorbance is measured as in the direct method.

Kjeldahl Method

- Direct Method with Preliminary Distillation to Remove Ammonia: A buffering compound is added to the sample and this solution is then distilled (boiled) to remove ammonia. Digestion reagents are then added to convert all organic nitrogen (urea) to ammonia, the solution is distilled, and the distillate is analyzed for ammonia either by direct nesslerization or by titration. The urea concentration is then calculated stoichiometrically from the measured ammonia concentration.

- Indirect Method: Two equal aliquots of sample are drawn. A buffering compound is added to the first aliquot and this solution is then distilled. The distillate is analyzed for ammonia. The digestion reagents are added to the second aliquot, converting organic nitrogen (urea) to ammonia. The solution is then distilled and this distillate is analyzed for ammonia. Urea concentration is calculated by subtracting ammonia nitrogen (first aliquot) from total nitrogen (second aliquot) and applying a stoichiometric conversion factor.

Both of the Kjeldahl urea analysis methods require that correction factors be applied to the urea and ammonia concentrations in order to account for the conversion of some urea to ammonia during distillation. The standard correction factor is: 7 percent of the urea content of the sample is converted to ammonia during distillation.[1] Thus, the urea concentrations should be increased by 7 percent, and the ammonia concentrations should be decreased by a stoichiometrically equivalent amount.

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(1) Standard Methods of Water and Wastewater Analysis, APHA, AWWA, WPCF, 14th edition, 1975, p. 408.

1.2.2 Ammonia Analysis Methods

Direct Nessler (or Direct Nesslerization) Method

The nessler reagent is added to the sample, and after full color development the absorbance of this solution is measured with a spectrophotometer. Absorbance is related to ammonia concentration through a calibration curve prepared from the absorbances of standard ammonia solutions.

Distillation Method

- Distillation and Nesslerization: A buffer is added to the sample and this solution is then distilled into a boric acid solution, leaving impurities and interferences behind. Nessler reagent is then added to the distillate which is then analyzed spectrophotometrically as in direct nesslerization.

- Distillation and Titration: The sample is distilled as in distillation and nesslerization, but into a boric acid solution containing a color indicator reagent. This distillate is then titrated with dilute sulfuric acid until the proper indicator color is obtained. Ammonia concentration is related to the volume of titrant used.

Specific Ion Electrode Method

The sample is pH adjusted with base, and the ammonia content is measured with an electrode calibrated specifically for ammonia. Electrode calibration is performed by immersing the electrode in a standard ammonia solution and noting the electrode meter reading.

1.3 Analytical Method Investigations

The urea analytical method investigations consisted of immediate and delayed analyses of field samples and prepared laboratory samples, utilizing several urea analysis procedures and preservative agents. The analysis investigations consisted specifically of the following:

1. Urea granulator scrubber outlet gas stream samples were analyzed within 24 hours of sample collection for urea and ammonia by TRC and by Agrico[1]. The TRC urea analyses were performed using the Kjeldahl direct method (with preliminary distillation); the Agrico urea analyses were performed using the Kjeldahl indirect method.

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(1) EPA Report 79-NHF-13a, "Process Emission Tests Performed at the Agrico Chemical Company Urea Manufacturing Facility, Blytheville, Arkansas." Prepared by TRC under EPA contract 68-02-2820, Work Assignment 11.

2. Two identical sets of twelve urea audit samples were prepared according to specific EPA instructions. One set was analyzed by TRC, the other by Agrico; both analyses took place within 12 hours of sample preparation. While both analyses were performed using the Kjeldahl total nitrogen method (without preliminary distillation), the final ammonia content (subsequently converted to urea) was determined by nesslerization by TRC, and by titration by Agrico.

The results and detailed descriptions of these two investigations are contained in the EPA report 79-NHF-13a, referenced above. The results are briefly summarized in Section 2.0 herein.

3. The Agrico scrubber outlet gas stream samples, preserved with mercuric chloride and sulfuric acid (each sample was divided into two portions), were returned to the TRC laboratory, and then analyzed periodically over 20 days for urea and ammonia. The urea analyses were performed using the direct Kjeldahl method with preliminary distillation.

4. Three pairs of identical urea samples were prepared by TRC according to specific EPA instructions. All of these laboratory samples were analyzed periodically for urea and ammonia, over 20 days, with the following qualifications: the first pair remained untreated; the second pair was preserved with mercuric chloride; the third pair was preserved with sulfuric acid. The direct Kjeldahl method with preliminary distillation was used for all urea analyses.

5. Five urea laboratory samples, prepared according to specific EPA instructions and each containing different amounts of ammonia, were analyzed by TRC for urea to evaluate the interfering effects of ammonia on the p-dimethylaminobenzaldehyde urea analysis method. All samples were analyzed within 24 hours of preparation.

6. The urea detection threshold of the p-dimethylaminobenzaldehyde method was evaluated by TRC using urea laboratory samples prepared according to specific EPA instructions.

7. Urea analyses performed during an emissions testing program were evaluated to investigate the interfering effects of sulfuric acid and the benefits of preliminary distillation on the p-dimethylaminobenzaldehyde method.

8. Prill tower scrubber outlet samples obtained during an emissions testing program were analyzed for urea and ammonia at TRC within 20 days of sample collection. Impinger contents and probe catches were analyzed individually in order to assess the sampling efficiency of the modified EPA particulate sampling train. The p-dimethylaminobenzaldehyde method with preliminary distillation was used for the urea analyses.

1.4 Description of Report Sections

The following sections of this report contain the Summary of Results and Conclusions (Section 2.0) and Discussion of Analysis Procedures (Section 3.0). Detailed information on methods and procedures and all laboratory data are contained in their associated appendices, as shown in the Table of Contents.

2.0 SUMMARY OF RESULTS AND CONCLUSIONS

This sections provides the results of the urea analytical method investigations performed over the period December 1978 through May 1980. The pertinent analysis results of the December 1978 emissions testing program at Agrico Chemical Company, Blytheville, Arkansas are briefly summarized in Sections 2.1 and 2.2. The results of all other investigations are presented in detail in Sections 2.3 through 2.7, and conclusions are presented in Section 2.8. The order of presentation in this section is generally chronological.

2.1 Comparison of TRC and Agrico Scrubber Outlet Gas Stream Analysis

The TRC and Agrico granulator C scrubber outlet analysis results are shown together in Tables 2-1 (urea results) and 2-2 (ammonia results). The TRC urea data were obtained directly using the Kjeldahl with preliminary distillation method. The Agrico urea data were obtained indirectly through separate Kjeldahl (total nitrogen) and distillation/titrimetric (ammonia nitrogen) analyses; urea was then calculated by subtracting ammonia nitrogen from total nitrogen. Both corrected and uncorrected data are shown in Tables 2-1 and 2-2 (corrected for conversion of urea to ammonia during distillation).

The urea data in Table 2-1 show that on the average the Agrico results are 30% higher than the TRC results. Run by run, however, there is no consistency between the TRC and Agrico data; the Agrico results vary from much higher to much lower than the TRC results. The indirect method of analysis used by Agrico is susceptible to inaccuracy, since errors in the component analyses (for total nitrogen and ammonia nitrogen) may be compounded when urea nitrogen is calculated by subtraction. Relatively small titrant volumes were used in the Agrico titration analyses: the total nitrogen titrant volumes ranged from 5.8 ml to 13.5 ml; the ammonia nitrogen titrant volumes ranged from 5.4 ml to

TABLE 2-1

TRC AND AGRICO UREA ANALYSIS RESULTS
FROM "C" GRANULATOR SCRUBBER OUTLET GAS-STREAM
AT AGRICO CHEMICAL COMPANY, BLYTHEVILLE, ARKANSAS

Run Number	Run 1				Run 2			
Date	12-18-78				12-19-78			
Volume of Gas Sampled (DSCF)[a]	34.93				34.44			
Volumetric Flowrate (DSCFM)[b]	55180				54720			
Production Rate (Tons/hour)	15.46				15.08			
Urea Analysis By:	TRC[c]		Agrico[d]		TRC		Agrico	
	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected
Total Sample Weight (Milligrams)	58.9	63.0	175.5	188.7	90.0	96.3	11.8	12.7
Grains/DSCF	0.02597	0.02779	0.07754	0.08338	0.04024	0.04306	0.00529	0.00569
Pounds/Hour	12.28	13.14	36.67	39.43	18.87	20.19	2.480	2.667
Pounds/Ton	0.794	0.850	2.372	2.551	1.251	1.339	0.164	0.176

Run Number	Run 3				Run 4			
Date	12-19-78				12-19-78			
Volume of Gas Sampled (DSCF)[a]	32.62				33.14			
Volumetric Flowrate (DSCFM)[b]	51130				52910			
Production Rate (Tons/hour)	15.08				15.08			
Urea Analysis By:	TRC[c]		Agrico[d]		TRC		Agrico	
	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected
Total Sample Weight (Milligrams)	33.6	36.0	26.4	28.3	48.1	51.5	104.8	112.7
Grains/DSCF	0.01586	0.01697	0.01249	0.01343	0.02235	0.02391	0.04880	0.05247
Pounds/Hour	6.951	7.438	5.474	5.886	10.14	10.85	22.13	23.80
Pounds/Ton	0.461	0.493	0.363	0.390	0.672	0.719	1.468	1.578

[a] Dry standard cubic feet @ 68°F, 29.92 inches Hg.

[b] Dry standard cubic feet per minute.

[c] TRC urea analysis by Kjeldahl with preliminary distillation. Corrected = uncorrected * 1.07.

[d] Agrico urea analysis by total Kjeldahl nitrogen minus ammonia nitrogen = urea nitrogen.

TABLE 2-1 (cont'd)

TRC AND AGRICO UREA ANALYSIS RESULTS
FROM "C" GRANULATOR SCRUBBER OUTLET GAS-STREAM
AT AGRICO CHEMICAL COMPANY, BLYTHEVILLE, ARKANSAS

Run Number	Run 5				Run 6			
Date	12-19-78				12-19-78			
Volume of Gas Sampled (DSCF)[a]	32.41				33.62			
Volumetric Flowrate (DSCFM)[b]	51730				53750			
Production Rate (Tons/hour)	15.08				15.08			
Urea Analysis By:	TRC[c]		Agrico[d]		TRC		Agrico	
	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected
Total Sample Weight (Milligrams)	28.8	30.8	19.7	21.2	47.0	50.3	60.3	64.8
Grains/DSCF	0.01368	0.01464	0.00938	0.01009	0.02153	0.02304	0.02768	0.02976
Pounds/Hour	6.067	6.492	4.159	4.472	9.917	10.61	12.75	13.71
Pounds/Ton	0.402	0.430	0.276	0.297	0.658	0.704	0.846	0.910

Run Number	Average			
Volume of Gas Sampled (DSCF)[a]	33.53			
Volumetric Flowrate (DSCFM)[b]	53237			
Production Rate (Tons/hour)	15.14			
Urea Analysis By:	TRC		Agrico	
	Uncorrected	Corrected	Uncorrected	Corrected
Total Sample Weight (Milligrams)	51.1	54.7	66.4	71.4
Grains/DSCF	0.02347	0.02511	0.03056	0.03286
Pounds/Hour	10.71	11.46	13.95	15.00
Pounds/Ton	0.707	0.757	0.921	0.990

[a]Dry standard cubic feet @ 68°F, 29.92 inches Hg.

[b]Dry standard cubic feet per minute.

[c]TRC urea analysis by Kjeldahl with preliminary distillation. Corrected = uncorrected * 1.07.

[d]Agrico urea analysis by total Kjeldahl nitrogen minus ammonia nitrogen = urea nitrogen.

TABLE 2-2

TRC AND AGRICO AMMONIA ANALYSIS RESULTS
FROM "C" GRANULATOR SCRUBBER OUTLET GAS-STREAM
AT AGRICO CHEMICAL COMPANY, BLYTHEVILLE, ARKANSAS

Run Number	Run 1					Run 2				
Date	12-18-78					12-19-78				
Volume of Gas Sampled (DSCF)[a]	34.93					34.44				
Volumetric Flowrate (DSCFM)[b]	55180					54720				
Production Rate (Tons/hour)	15.46					15.08				
Ammonia Analysis By:	TRC[c]			Agrico[d]		TRC			Agrico	
	DN	Dist.-N Uncorrected	Dist.-N Corrected	Dist.-T Uncorrected	Dist.-T Corrected	DN	Dist.-N Uncorrected	Dist.-N Corrected	Dist.-T Uncorrected	Dist.-T Corrected
Total Sample Weight (Milligrams)	403.7	423.2	420.7	464.1	456.6	332.6	328.2	324.4	484.7	484.2
Grains/DSCF	0.1780	0.1866	0.1855	0.2050	0.2017	0.1487	0.1468	0.1451	0.2172	0.2170
Pounds/Hour	84.17	88.24	87.72	96.98	95.41	69.74	68.82	68.02	101.9	101.8
Pounds/Ton	5.444	5.708	5.674	6.273	6.172	4.625	4.564	4.511	6.755	6.748

Run Number	Run 3					Run 4				
Date	12-19-78					12-19-78				
Volume of Gas Sampled (DSCF)[a]	32.62					33.14				
Volumetric Flowrate (DSCFM)[b]	51130					52910				
Production Rate (Tons/hour)	15.08					15.08				
Ammonia Analysis By:	TRC			Agrico		TRC			Agrico	
	DN	Dist.-N Uncorrected	Dist.-N Corrected	Dist.-T Uncorrected	Dist.-T Corrected	DN	Dist.-N Uncorrected	Dist.-N Corrected	Dist.-T Uncorrected	Dist.-T Corrected
Total Sample Weight (Milligrams)	369.6	592.9	591.5	381.5	380.4	362.8	348.2	346.2	369.4	364.9
Grains/DSCF	0.1745	0.2799	0.2792	0.1805	0.1800	0.1686	0.1618	0.1609	0.1720	0.1699
Pounds/Hour	76.46	122.65	122.36	79.10	78.9	76.45	73.37	72.95	78.01	77.06
Pounds/Ton	5.070	8.133	8.114	5.245	5.230	5.070	4.865	4.837	5.173	5.110

[a] Dry standard cubic feet @ 68°F, 29.92 inches Hg.

[b] Dry standard cubic feet per minute.

[c] TRC ammonia analysis done by direct nesslerization (DN) and distillation/nesslerization (Dist.-N). Correction is for urea to ammonia conversion. Corrected = uncorrected - 0.07 * corrected urea/1.765.

[d] Agrico ammonia analysis done by distillation/titration (Dist.-T). Correction is for urea to ammonia conversion.

TABLE 2-2 (cont'd)

TRC AND AGRICO AMMONIA ANALYSIS RESULTS
FROM "C" GRANULATOR SCRUBBER OUTLET GAS-STREAM
AT AGRICO CHEMICAL COMPANY, BLYTHEVILLE, ARKANSAS

Run Number	Run 5					Run 6				
Date	12-19-78					12-19-78				
Volume of Gas Sampled (DSCF)[a]	32.41					33.62				
Volumetric Flowrate (DSCFM)[b]	51730					53750				
Production Rate (Tons/hour)	15.08					15.08				
Ammonia Analysis by:	TRC[c]			Agrico[d]		TRC			Agrico	
	DN	Dist.-N Uncorrected	Dist.-N Corrected	Dist.-T Uncorrected	Dist.-T Corrected	DN	Dist.-N Uncorrected	Dist.-N Corrected	Dist.-T Uncorrected	Dist.-T Corrected
Total Sample Weight (Milligrams)	341.6	321.9	320.7	353.7	352.9	301.5	305.5	303.5	300.7	298.1
Grains/DSCF	0.1623	0.1530	0.1524	0.1684	0.1680	0.1381	0.1399	0.1390	0.1380	0.1368
Pounds/Hour	71.96	67.81	67.56	74.68	74.51	63.62	64.46	64.04	63.59	63.04
Pounds/Ton	4.772	4.497	4.480	4.952	4.941	4.219	4.275	4.247	4.217	4.181

Run Number	Average				
Volume of Gas Sampled (DSCF)[a]	33.53				
Volumetric Flowrate (DSCFM)[b]	53237				
Production Rate (Tons/hour)	15.14				
Ammonia Analysis By:	TRC[c]			Agrico[d]	
	DN	Dist.-N Uncorrected	Dist.-N Corrected	Dist.-T Uncorrected	Dist.-T Corrected
Total Sample Weight (Milligrams)	352.0	386.7	384.5	392.4	389.6
Grains/DSCF	0.1617	0.1776	0.1766	0.1806	0.1793
Pounds/Hour	73.76	81.03	80.57	82.41	81.82
Pounds/Ton	4.872	5.352	5.322	5.465	5.426

[a]Dry standard cubic feet @ 68°F, 29.92 inches Hg.

[b]Dry standard cubic feet per minute.

[c]TRC ammonia analysis done by direct nesslerization (DN) and distillation/nesslerization (Dist.-N). Correction is for urea to ammonia conversion. Corrected = uncorrected - 0.07 * corrected urea/1.765.

[d]Agrico ammonia analysis done by distillation/titration (Dist.-T). Correction is for urea to ammonia converstion.

11.5 ml. In order to minimize titration errors, TRC has found that titrant volumes of at least 20 ml should be used.

The ammonia data in Table 2-2 show that on the average the TRC and Agrico results are in close agreement. TRC utilized two analysis methods: direct nesslerization and nesslerization with preliminary distillation. Agrico utilized the titration with preliminary distillation method.

2.2 Urea Audit Samples - Comparison of TRC and Agrico Analyses

TRC and Agrico each analyzed a different set of 12 urea samples, each set prepared according to specific EPA instructions. Both analyses were performed at the Agrico laboratory within 12 hours of sample preparation. The TRC audit sample set was analyzed using the total Kjeldahl nitrogen method with no preliminary distillation, ending with nesslerization. The Agrico audit sample set was analyzed using the same total Kjeldahl nitrogen method, but ending with titration. The results of the urea audit sample analyses are shown in Table 2-3.

The TRC analysis results average 6.0 percent lower than the actual urea sample weights, and each sample analysis is less than the actual. It was initially thought that the consistently low results were due to the blank correction. Discounting the blank correction in the analysis calculation, however, yields an overall +5.0 percent error. This indicates that factors other than the blank correction may also be involved in the consistently low (blank corrected) results.

The Agrico analysis results average 92.9 percent higher than the actual urea sample weights. These analyses were concluded with titration, and very low titration volumes were often used (7 of the 12 titrations required less than 6 ml of titrant). Larger titrant volumes (at least 20 ml) are necessary

TABLE 2-3

RESULTS OF UREA AUDIT SAMPLE ANALYSES
PERFORMED BY TRC AND AGRICO
AT AGRICO CHEMICAL COMPANY, BLYTHEVILLE, ARKANSAS

Audit Sample	TRC Analysis*			AGRICO Analysis**			
	Actual Urea Sample Weight (mg)	As Measured (mg)	Error [a] (%)	Actual Urea Sample Weight (mg)	Measured As Nitrogen (mg)	Equivalent Urea [b] (mg)	Error [c] (%)
	A	B		C	D	E	
1	100.71	94.04	-6.6	100.54	96.3	206.4	105
2	311.98	288.90	-7.4	292.78	281.1	602.4	106
3	598.36	568.75	-4.9	598.08	582.4	1248.0	109
4	5.64	5.44	-3.5	5.26	3.6	7.7	46.4
5	11.60	11.15	-3.9	9.64	11.8	25.3	162
6	40.40	38.69	-4.2	42.48	38.6	82.7	94.7
7	2.60	2.43	-6.5	2.04	1.1	2.4	17.6
8	6.84	6.49	-5.1	6.16	5.0	10.7	73.7
9	9.42	8.96	-4.9	9.54	9.5	20.4	114
10	5.40	4.90	-9.3	5.96	5.3	11.4	91.3
11	4.30	3.93	-8.6	4.18	3.9	8.4	101
12	30.16	27.93	-7.4	31.32	27.4	58.7	87.4
Average			-6.0				92.9

[a] Percent error = (100 * B/A) - 100

[b] E = D * 60/28

[c] Percent error = (100 * E/C) - 100

* TRC Analysis by total Kjeldahl nitrogen method, ending with Nesslerization. No preliminary distillation.
** Agrico analysis by total Kjeldahl nitrogen method, ending with Titration. No preliminary distillation.

in order to help minimize errors during titration. A disadvantage of the titration method is that the entire sample is used for one titration; consequently, if an error is made or if a result is suspect, there is no possibility of re-analysis.

2.3 Preservation of Urea Samples

Two different groups of urea sample solutions were analyzed over time in order to assess the stabilizing effects of mercuric chloride ($HgCl_2$) and sulfuric acid (H_2SO_4) on the urea and ammonia content of the samples. The granulator C scrubber outlet gaseous samples (obtained from the Agrico December 1978 emission testing program) and six specially prepared laboratory urea samples were analyzed at TRC in this manner. The urea analyses were performed with the direct Kjeldahl method with preliminary distillation. The results of these preservation analyses are as follows.

2.3.1 Granulator C Scrubber Outlet Gas Stream Sample Preservation

After the initial urea and ammonia analyses were performed at Agrico on the granulator C scrubber outlet gas steam samples, the samples were divided into two portions. To one portion was added saturated $HgCl_2$ solution (approximately 2 ml per liter of sample); to the other portion was added concentrated sulfuric acid (approximately 2 ml per liter of sample). These portions were returned to TRC and then analyzed for urea and ammonia, starting 6-7 days after the initial field analysis and then every 2-3 days through a 2-week period (for a total of six analyses of each sample portion, including the initial field sample). The urea analyses were performed using the direct Kjeldahl with preliminary distillation method (finishing with nesslerization). The ammonia analyses were performed with two methods: direct

nesslerization and nesslerization with preliminary distillation.

The results of these analyses are shown in Tables 2-4 through 2-9. The urea and distilled ammonia data include as-measured values and values corrected for urea-to-ammonia conversion during distillation, using the standard 7 percent correction factor.[1] Nearly all the samples exhibit occasional large fluctuations in measured urea or ammonia content. These fluctuations often interrupt or reverse what, in some instances, initially may appear to be progressive changes in urea or ammonia content. Reasons for these large positive and negative fluctuations are not evident, and overall there are no discernable trends in the data. Graphs of the corrected urea and ammonia data in Tables 2-4 through 2-9 are contained in Appendix C.

Least-squares linear regressions were performed on the corrected urea and ammonia data in order to quantify the degree of correlation between the urea or ammonia content of a sample and time of analysis. The calculated coefficients for each set of data are shown in Table 2-10. In general, the urea correlation coefficients indicate there is little relationship between time and urea content of the samples, for either preservative agent.

The $HgCl_2$-preserved ammonia analysis results indicate a general trend of ammonia content decreasing with time. The H_2SO_4-preserved ammonia analysis results show no general change or trend.

Further corroboration of the stability of urea field samples was obtained during a sampling program conducted by TRC in April 1980.[2] Two series of

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(1) Standard Methods of Water and Wastewater Analysis, APHA, AWWA, WPCF, 14th edition, 1975, p. 408

(2) EPA Report 80-NFH-14, "Process Emission Tests at the Reichhold Chemicals Inc. Urea Manufacturing Facility, St. Helens, Oregon". Prepared by TRC under EPA contract 68-02-2820, Work Assignment 19.

TABLE 2-4

AGRICO GRANULATOR C SCRUBBER OUTLET GASEOUS SAMPLE PRESERVATION

TEST RUN NUMBER 1

Preservative	Day	Direct Ammonia[a] (mg)	Distilled Ammonia[b] (mg) As Measured	Distilled Ammonia[b] (mg) Corrected[c]	Urea[d] (mg) As Measured	Urea[d] (mg) Corrected[e]
$HgCl_2$	0	404	423	421	58.9	63.0
	7	NA	507	503	97.2	104.0
	10	NA	422	419	70.9	75.9
	15	419	389	385	93.8	100.4
	17	478	424	420	91.2	97.6
	21	444	429	425	86.0	92.0
H_2SO_4	0	404	423	421	58.9	63.0
	7	NA	453	450	72.2	77.3
	10	NA	*	*	*	*
	15	497	462	459	77.4	82.8
	17	488	529	526	81.7	87.4
	21	470	507	504	75.7	81.0

a Direct Nessler Analysis method.
b Nessler with preliminary distillation analysis method.
c Corrected for urea to ammonia conversion. Corrected = uncorrected - 0.07* corrected urea/1.765.
d Kjeldahl with preliminary distillation analysis method.
e Corrected for urea to ammonia conversion. Corrected = uncorrected * 1.07.
NA Not Analyzed.
* Suspect and not used.

TABLE 2-5

AGRICO GRANULATOR C SCRUBBER OUTLET GASEOUS SAMPLE PRESERVATION

TEST RUN NUMBER 2

Preservative	Day	Direct Ammonia[a] (mg)	Distilled Ammonia[b] (mg) As Measured	Distilled Ammonia[b] (mg) Corrected[c]	Urea[d] (mg) As Measured	Urea[d] (mg) Corrected[e]
$HgCl_2$	0	333	328	324	90.0	96.3
	6	NA	312	309	77.7	83.1
	9	NA	270	266	84.5	90.4
	14	307	313	310	82.1	87.8
	16	361	285	282	79.5	85.1
	20	332	173	169	85.6	91.6
H_2SO_4	0	333	328	324	90.0	96.3
	6	NA	351	348	77.7	83.1
	9	NA	*	*	*	*
	14	327	335	330	110	118
	16	500	314	311	76.9	82.3
	20	361	332	329	73.4	78.5

a Direct Nessler Analysis method.
b Nessler with preliminary distillation analysis method.
c Corrected for urea to ammonia conversion. Corrected = uncorrected - 0.07* corrected urea/1.765.
d Kjeldahl with preliminary distillation analysis method.
e Corrected for urea to ammonia conversion. Corrected = uncorrected * 1.07.
NA Not Analyzed.
* Suspect and not used.

TABLE 2-6

AGRICO GRANULATOR C SCRUBBER OUTLET GASEOUS SAMPLE PRESERVATION

TEST RUN NUMBER 3

Preservative	Day	Direct Ammonia[a] (mg)	Distilled Ammonia[b] (mg) As Measured	Distilled Ammonia[b] (mg) Corrected[c]	Urea[d] (mg) As Measured	Urea[d] (mg) Corrected[e]
$HgCl_2$	0	370	593	592	33.6	36.0
	6	NA	341	341	*	*
	9	NA	350	349	26.2	28.0
	14	358	342	341	25.0	26.8
	16	476	303	302	33.8	36.2
	20	369	215	214	27.4	29.3
H_2SO_4	0	370	593	592	33.6	36.0
	6	NA	369	368	26.1	27.9
	9	NA	350	349	19.4	20.6
	14	338	378	378	6.6	7.1
	16	429	349	347	38.1	40.8
	20	374	363	362	25.8	27.6

a Direct Nessler Analysis method.
b Nessler with preliminary distillation analysis method.
c Corrected for urea to ammonia conversion. Corrected = uncorrected - 0.07* corrected urea/1.765.
d Kjeldahl with preliminary distillation analysis method.
e Corrected for urea to ammonia conversion. Corrected = uncorrected * 1.07.
NA Not Analyzed.
* Suspect and not used.

TABLE 2-7

AGRICO GRANULATOR C SCRUBBER OUTLET GASEOUS SAMPLE PRESERVATION

TEST RUN NUMBER 4

Preservative	Day	Direct Ammonia[a] (mg)	Distilled Ammonia[b] (mg) As Measured	Distilled Ammonia[b] (mg) Corrected[c]	Urea[d] (mg) As Measured	Urea[d] (mg) Corrected[e]
$HgCl_2$	0	363	348	346	48.1	51.5
	6	NA	330	328	45.4	48.6
	9	NA	325	324	32.5	34.8
	14	308	333	332	21.2	22.7
	16	403	310	309	19.7	21.1
	20	354	206	204	40.1	42.9
H_2SO_4	0	363	348	346	48.1	51.5
	6	NA	359	357	49.8	53.4
	9	NA	333	331	43.1	46.1
	14	349	401	400	32.5	34.8
	16	398	395	394	23.3	24.9
	20	420	342	340	39.0	41.7

a Direct Nessler Analysis method.
b Nessler with preliminary distillation analysis method.
c Corrected for urea to ammonia conversion. Corrected = uncorrected - 0.07* corrected urea/1.765.
d Kjeldahl with preliminary distillation analysis method.
e Corrected for urea to ammonia conversion. Corrected = uncorrected * 1.07.
NA Not Analyzed.
* Suspect and not used.

TABLE 2-8

AGRICO GRANULATOR C SCRUBBER OUTLET GASEOUS SAMPLE PRESERVATION

TEST RUN NUMBER 5

Preservative	Day	Direct Ammonia[a] (mg)	Distilled Ammonia[b] (mg) As Measured	Distilled Ammonia[b] (mg) Corrected[c]	Urea[d] (mg) As Measured	Urea[d] (mg) Corrected[e]
$HgCl_2$	0	342	322	321	28.8	30.8
	6	NA	307	306	28.3	30.3
	9	NA	326	326	9.9	10.6
	14	301	299	298	13.5	14.4
	16	334	276	274	38.1	40.8
	20	329	198	197	16.4	17.5
H_2SO_4	0	342	322	321	28.8	30.8
	6	NA	*	*	*	*
	9	NA	367	367	5.8	6.2
	14	318	294	293	21.3	22.8
	16	372	312	311	15.1	16.2
	20	367	329	328	15.1	16.2

a Direct Nessler Analysis method.
b Nessler with preliminary distillation analysis method.
c Corrected for urea to ammonia conversion. Corrected = uncorrected - 0.07* corrected urea/1.765.
d Kjeldahl with preliminary distillation analysis method.
e Corrected for urea to ammonia conversion. Corrected = uncorrected * 1.07.
NA Not Analyzed.
* Suspect and not used.

TABLE 2-9

AGRICO GRANULATOR C SCRUBBER OUTLET GASEOUS SAMPLE PRESERVATION

TEST RUN NUMBER 6

Preservative	Day	Direct Ammonia[a] (mg)	Distilled Ammonia[b] (mg) As Measured	Distilled Ammonia[b] (mg) Corrected[c]	Urea[d] (mg) As Measured	Urea[d] (mg) Corrected[e]
$HgCl_2$	0	302	306	304	47.0	50.3
	7	NA	276	274	44.3	47.4
	9	NA	286	285	27.8	29.7
	14	271	240	240	4.6	4.9
	16	296	251	249	37.3	39.9
	20	284	183	181	38.7	41.4
H_2SO_4	0	302	306	304	47.0	50.3
	7	NA	296	295	33.9	36.3
	9	NA	289	288	12.8	13.7
	14	281	275	275	*	*
	16	317	NA	NA	NA	NA
	20	312	317	316	31.0	33.2

a Direct Nessler Analysis method.
b Nessler with preliminary distillation analysis method.
c Corrected for urea to ammonia conversion. Corrected = uncorrected - 0.07* corrected urea/1.765.
d Kjeldahl with preliminary distillation analysis method.
e Corrected for urea to ammonia conversion. Corrected = uncorrected * 1.07.
NA Not Analyzed.
* Suspect and not used.

TABLE 2-10

LEAST-SQUARES LINEAR REGRESSION RESULTS
AGRICO GRANULATOR C SCRUBBER OUTLET GASEOUS SAMPLE PRESERVATION

Concentration (ppm) = M * time (days) + b

		UREA**			AMMONIA**		
Preservative	Test Run	Slope m	Intercept b	Correlation Coefficient r	Slope m	Intercept b	Correlation Coefficient r
$HgCl_2$	1	1.277	73.9	0.6040	-1.626	448	-0.3147
	2	-0.201	91.2	-0.3071	-5.667	338	-0.7273
	3	-0.219	33.8	-0.3745	-15.480	524	-0.8947
	4	-1.067	48.5	-0.5983	-5.323	365	-0.7459
	5	-0.312	27.4	-0.1947	-5.245	344	-0.7984
	6	-0.842	44.9	-0.3619	-5.531	316	-0.9129
H_2SO_4	1	0.957	66.8	0.8681	4.370	420	0.8682
	2	-0.362	95.7	-0.1805	-0.485	334	-0.2939
	3	-0.288	29.8	-0.1762	-9.529	503	-0.7292
	4	-0.003	42.3	-0.0471	1.278	347	0.3211
	5	-0.548	24.9	-0.4630	-0.739	333	-0.2075
	6	-0.777	40.4	-0.4271	0.208	294	0.1044

**Corrected for urea to ammonia conversion during distillation.

emissions test runs were performed on the outlet of a prill tower scrubber. The urea content of these samples was analyzed in the field (within 24 hours of sample collection) and at TRC up to 16 days later. Urea analyses were performed with the p-dimethylaminobenzaldehyde method (with preliminary distillation). The average impinger catches for each test series were as follows:

	Average Impinger Catch (mg)	
	TRC Analysis	Field Analysis
Series A (2 runs)	19.1	18.8
Series B (3 runs)	12.0	13.1
Average	14.8	15.4

These data show an insignificant average difference between the field and TRC analyses. Complete details of this emissions testing program are contained in EPA Report 80-NHF-14.

2.3.2 Preservation of Laboratory Urea Samples

Six urea sample solutions were prepared and analyzed periodically over 19 days in order to determine the effect of mercuric chloride ($HgCl_2$) and sulfuric acid (H_2SO_4) as preservative agents. The six sample solutions were as follows:

Sample	Urea (ppm)	Preservative Added
A	40	None
B	100	None
C	40	2 ml saturated $HgCl_2$/liter
D	100	5 ml saturated $HgCl_2$/liter
E	40	2 ml concentrated H_2SO_4/liter
F	100	5 ml concentrated H_2SO_4/liter

These solutions were analyzed for urea and ammonia every 2 to 3 days over a period of 19 days (a total of 9 analyses). Separate blanks containing the

appropriate preservative agent but no urea were prepared and analyzed as well. The urea analyses were performed using the direct Kjeldahl with preliminary distillation method. The ammonia analyses were performed using both the direct nessler method and the nessler with preliminary distillation method. The correction for conversion of urea to ammonia during distillation was applied to the urea and distilled nessler ammonia results. The analysis data for all six solutions (A through F) are shown in Tables 2-11 through 2-16, respectively.

None of these solutions, including the "unpreserved" solutions A and B, showed any detectable change in urea or ammonia with time. Because of this clear consistency, no linear regressions were performed. Each solution exhibited small fluctuations in urea and ammonia concentration from analysis to analysis; but these fluctuations can be considered within the resolution of the analysis methods. Some of the fluctuations (positive and negative) may also be due to small changes in reagent characteristics or analyst technique. Evidence of this may be the consistently "low" urea and ammonia concentrations measured on Day 8.

The direct nessler ammonia concentrations are always less than the distilled nessler ammonia concentrations. The differences are small (approximately 1-2 ppm) and may be due to slight, normally insignificant interferences introduced by the distillation procedure. In addition, the distilled ammonia data may reflect some urea converted to ammonia during distillation.

The standard 7 percent correction applied to the urea and ammonia results (in order to account for urea converted to ammonia during distillation) appears reasonable for the urea data, but is clearly inappropriate for the ammonia data. Negative ammonia concentrations result from this correction

TABLE 2-11

LABORATORY UREA SAMPLE PRESERVATION ANALYSIS RESULTS
SOLUTION A: 40 PPM UREA, NO PRESERVATIVES

Day	Direct Ammonia (ppm)[a]	Distilled Ammonia (ppm)[b] As Measured	Distilled Ammonia (ppm)[b] Corrected[c]	Urea (ppm)[d] As Measured	Urea (ppm)[d] Corrected[e]
0	0	2.2	0.7	35.3	37.8
1	NA	0	*	34.9	37.3
4	NA	0.6	*	38.2	40.9
6	0.1	0	*	37.9	40.6
8	0	0.4	*	34.0	36.4
11	0.1	0.7	*	36.8	39.4
13	0.1	0.8	*	37.6	40.2
15	0.3	1.2	*	37.0	39.6
18	0	1.1	*	37.6	40.2

a Direct Nessler Analysis Method.
b Nessler with preliminary distillation analysis method.
c Corrected for urea to ammonia conversion. Corrected = uncorrected - 0.07 * corrected urea/1.765.
d Kjeldahl with preliminary distillation analysis method.
e Corrected for urea to ammonia conversion. Corrected = uncorrected * 1.07.
NA Not analyzed.
* Less than zero.

TABLE 2-12

LABORATORY UREA SAMPLE PRESERVATION ANALYSIS RESULTS
SOLUTION B: 100 PPM UREA, NO PRESERVATIVES

Day	Direct Ammonia (ppm)[a]	Distilled Ammonia (ppm)[b] As Measured	Distilled Ammonia (ppm)[b] Corrected[c]	Urea (ppm)[d] As Measured	Urea (ppm)[d] Corrected[e]
0	0	2.4	*	90.6	96.9
1	NA	0	*	92.7	99.2
4	NA	1.4	*	94.3	100.9
6	0.2	1.2	*	93.1	99.6
8	0.2	1.4	*	81.6	87.3
11	0.4	1.6	*	91.5	97.9
13	0.3	2.0	*	90.3	96.6
15	0.1	2.5	*	92.6	99.1
18	0.2	2.6	*	91.4	97.8

a Direct Nessler Analysis Method.
b Nessler with preliminary distillation analysis method.
c Corrected for urea to ammonia conversion. Corrected = uncorrected - 0.07 * corrected urea/1.765.
d Kjeldahl with preliminary distillation analysis method.
e Corrected for urea to ammonia conversion. Corrected = uncorrected * 1.07.
NA Not analyzed.
* Less than zero.

TABLE 2-13

LABORATORY UREA SAMPLE PRESERVATION ANALYSIS RESULTS
SOLUTION C: 40 PPM UREA, $HgCl_2$ PRESERVATIVE

Day	Direct Ammonia (ppm)[a]	Distilled Ammonia (ppm)[b] As Measured	Distilled Ammonia (ppm)[b] Corrected[c]	Urea (ppm)[d] As Measured	Urea (ppm)[d] Corrected[e]
0	0	2.1	0.6	35.9	38.4
1	NA	0.7	*	35.6	38.1
4	NA	0.8	*	37.9	40.6
6	0.1	2.8	1.2	37.5	40.1
8	0	0.9	*	35.9	38.4
11	0.2	1.3	*	38.0	40.7
13	0	1.3	*	38.9	41.6
15	0.2	0.9	*	39.8	42.6
18	0	0.9	*	38.1	40.8

a Direct Nessler Analysis Method.
b Nessler with preliminary distillation analysis method.
c Corrected for urea to ammonia conversion. Corrected = uncorrected - 0.07 * corrected urea/1.765.
d Kjeldahl with preliminary distillation analysis method.
e Corrected for urea to ammonia conversion. Corrected = uncorrected * 1.07.
NA Not analyzed.
* Less than zero.

TABLE 2-14

LABORATORY UREA SAMPLE PRESERVATION ANALYSIS RESULTS
SOLUTION D: 100 PPM UREA, $HgCl_2$ PRESERVATIVE

Day	Direct Ammonia (ppm)[a]	Distilled Ammonia (ppm)[b] As Measured	Distilled Ammonia (ppm)[b] Corrected[c]	Urea (ppm)[d] As Measured	Urea (ppm)[d] Corrected[e]
0	0	2.2	*	97.2	104.0
1	NA	1.2	*	91.0	97.4
4	NA	1.6	*	94.8	101.4
6	0.1	1.6	*	93.3	99.8
8	0	1.6	*	86.4	92.4
11	0	1.0	*	91.8	98.2
13	0	2.4	*	93.1	99.6
15	0.2	2.1	*	92.8	99.3
18	0	2.4	*	95.0	101.7

a Direct Nessler Analysis Method.
b Nessler with preliminary distillation analysis method.
c Corrected for urea to ammonia conversion. Corrected = uncorrected - 0.07 * corrected urea/1.765.
d Kjeldahl with preliminary distillation analysis method.
e Corrected for urea to ammonia conversion. Corrected = uncorrected * 1.07.
NA Not analyzed.
* Less than zero.

TABLE 2-15

LABORATORY UREA SAMPLE PRESERVATION ANALYSIS RESULTS
SOLUTION E: 40 PPM UREA, H_2SO_4 PRESERVATIVE

Day	Direct Ammonia (ppm)[a]	Distilled Ammonia (ppm)[b] As Measured	Distilled Ammonia (ppm)[b] Corrected[c]	Urea (ppm)[d] As Measured	Urea (ppm)[d] Corrected[e]
0	0	0.2	*	35.3	37.8
1	NA	0.3	*	35.8	38.3
4	NA	0.6	*	38.1	40.8
6	0.2	0.5	*	37.7	40.3
8	0.1	0.6	*	34.3	36.7
11	0	0.6	*	36.1	38.6
13	0	0.6	*	37.4	40.0
15	0	0.8	*	37.8	40.4
18	0	0.5	*	38.8	41.5

a Direct Nessler Analysis Method.
b Nessler with preliminary distillation analysis method.
c Corrected for urea to ammonia conversion. Corrected = uncorrected - 0.07 * corrected urea/1.765.
d Kjeldahl with preliminary distillation analysis method.
e Corrected for urea to ammonia conversion. Corrected = uncorrected * 1.07.
NA Not analyzed.
* Less than zero.

TABLE 2-16

LABORATORY UREA SAMPLE PRESERVATION ANALYSIS RESULTS
SOLUTION F: 100 PPM UREA, H_2SO_4 PRESERVATIVE

Day	Direct Ammonia (ppm)[a]	Distilled Ammonia (ppm)[b] As Measured	Distilled Ammonia (ppm)[b] Corrected[c]	Urea (ppm)[d] As Measured	Urea (ppm)[d] Corrected[e]
0	0	2.1	*	90.6	96.9
1	NA	1.3	*	95.6	102.3
4	NA	1.9	*	93.7	100.3
6	0	2.1	*	94.9	101.5
8	0	2.8	*	92.3	98.9
11	0	2.7	*	91.7	98.1
13	0	2.9	*	91.9	98.3
15	0.1	1.8	*	81.9	87.6
18	0	1.6	*	96.2	102.9

a Direct Nessler Analysis Method.
b Nessler with preliminary distillation analysis method.
c Corrected for urea to ammonia conversion. Corrected = uncorrected - 0.07 * corrected urea/1.765.
d Kjeldahl with preliminary distillation analysis method.
e Corrected for urea to ammonia conversion. Corrected = uncorrected * 1.07.
NA Not analyzed.
* Less than zero.

because the urea concentrations are relatively much higher than the ammonia concentrations and because the ammonia concentrations are themselves absolutely low.

2.4 Ammonia Interference on Urea Analysis

TRC prepared standard urea solutions containing known amounts of ammonia in order to assess the interfering effects of ammonia on the p-dimethylaminobenzaldehyde urea analysis method (with no preliminary distillation). A urea calibration curve was first prepared with urea solutions ranging from zero to 200 ppm. Five additional solutions were then prepared, each containing 100 ppm urea and 100 to 1000 ppm ammonia (as ammonium chloride). The absorbance of each of these sample solutions was then read and then converted to urea concentration using the prepared calibration curve. The indicated urea concentrations and related data are shown in Table 2-17. A plot of ammonia/urea molar ratio vs. urea analysis error is shown in Figure 2-1.

These data indicate that an ammonia/urea molar ratio of about 3.5 will yield a 1% positive error in the urea analysis, and a molar ratio of about 20 will yield a 3% positive error. These ammonia effects are only slightly greater than the effects stated in the article that introduced the p-dimethylaminobenzaldehyde urea analysis method: "Ammonium chloride does not interfere when present in a 10 to 1 mole ratio and introduces only a 1% relative error when the mole ratio is 15".[1] The first two ammonia/urea solutions (100 ppm and 500 ppm ammonia) gave absorbances only slightly greater than the standard 100 ppm urea solution (see Appendix D). These differences

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(1) Watt, G.W. and J.D. Chrisp, "Spectrophotometric Method for Determination of Urea", Analytical Chemistry, Volume 26, 1954, pp. 452-453.

TABLE 2-17

RESULTS OF INTERFERENCE EFFECTS OF AMMONIA ON UREA ANALYSIS*

Actual Ammonia Concentration(ppm)	Actual Urea Concentration(ppm) B	Mole Ratio** Urea/Ammonia	Indicated Urea Concentration(ppm) C	Percent Error***
100	100	3.52	101	+ 1
500	100	17.60	102	+ 2
1000	100	35.21	106	+ 6
5000	100	176.0	130	+ 30
10000	100	352.1	151	+ 51

* p-dimethylaminobenzaldehyde analysis method (no preliminary distillation)

** 100 ppm urea = 100 mg/liter = 0.00167 M
100 ppm ammonia = 100 mg/liter = 0.00588 M

*** percent error = 100 * (C-B)/B

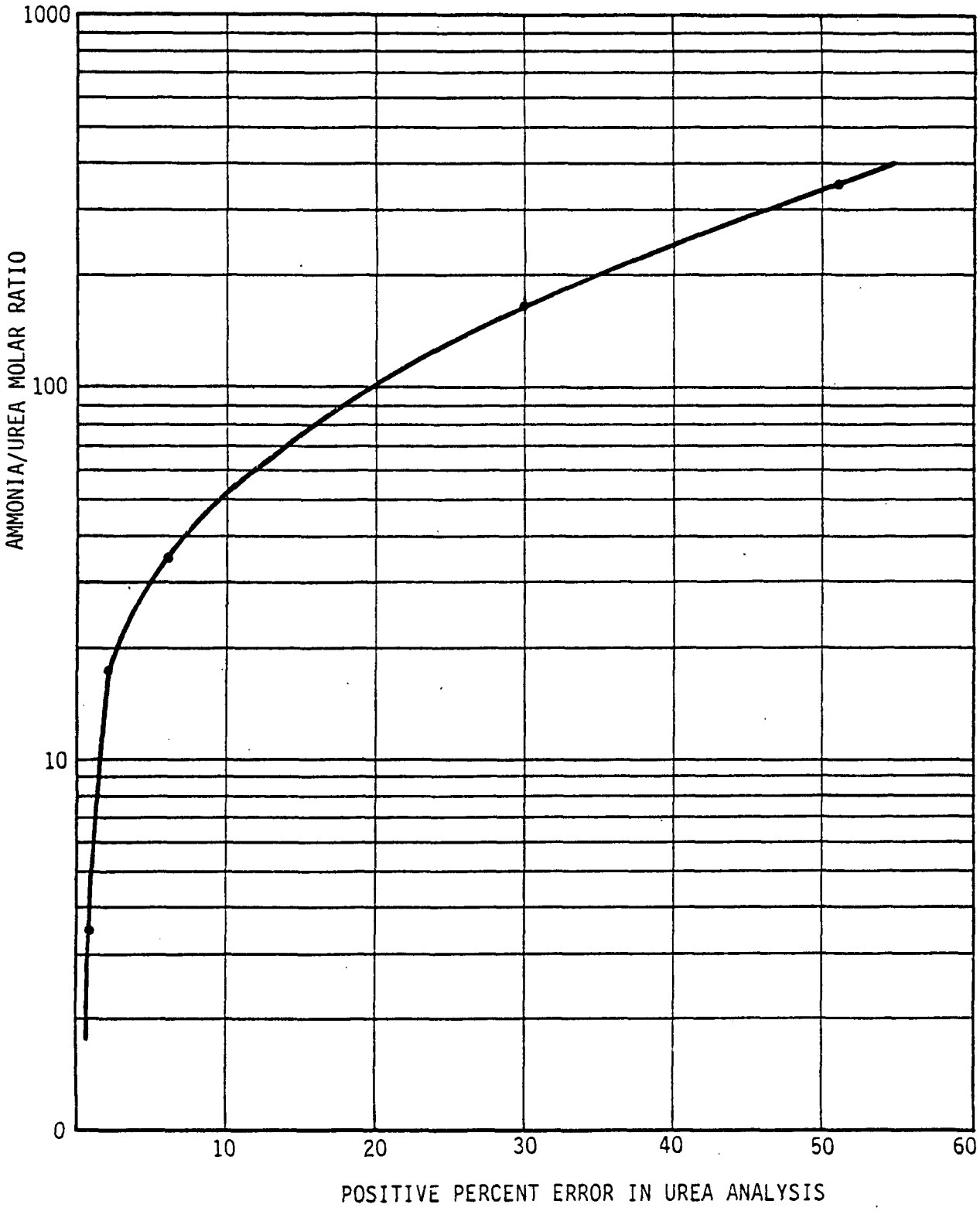

FIGURE 2-1: INTERFERENCE EFFECTS OF AMMONIA ON UREA ANALYSIS

0988-001

can be considered within the precision limits of the analysis method and, on this basis, the TRC data generally corroborate the ammonia interference effects stated by Watt and Chrisp.

2.5 Evaluation of Standard Procedures for the Proposed EPA Urea Analytical Method

Emissions testing was performed by TRC on prill tower scrubbers at a urea manufacturing plant during August 1979.[1] Additional urea analysis investigations were performed by TRC during the analysis of the samples collected during this test program. These investigations were performed in order to evaluate two aspects of the p-dimethylaminobenzaldehyde (PDAB) urea analysis method: preliminary distillation (to remove ammonia) and the effect of sulfuric acid as an interference. The results of these investigations are as follows.

2.5.1 Effects of Preliminary Distillation

Urea-in-mannitol audit samples were prepared by EPA and given to TRC for analysis in order to assess the accuracy of the p-dimethylaminobenzaldehyde urea analysis method for this test program. The samples were dissolved in 100 mls of water, and a portion of each of these audit sample solutions was first distilled and then analyzed for urea; another portion was analyzed without any preliminary distillation (direct analysis). Distilled and undistilled standard urea solutions were prepared and the audit sample solutions were read against the standard solution calibration curves. The purpose of the investigation was to evaluate the effect of the preliminary (ammonia-removing)

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(1) EPA Report 78-NHF-3, "Process Emissions Tests at the W.R. Grace and Co. Urea Manufacturing Facility in Memphis, Tennessee". Prepared by TRC under EPA Contract No. 68-02-2820, Work Assignment No. 9.

distillation on the indicated urea content of samples. The results of the analyses and comparisons are shown in Table 2-18.

Audit sample number 4 aside, these data show that comparison of distilled samples to distilled standards (column A) and comparison of direct samples to direct standards (column C) both yield small errors (within 5% on the average). However, comparison of distilled samples to direct standards (column B) yields relatively large errors (about 14%).

The column A and column C data indicate that it makes no difference whether you distill or not, as long as both samples and standards are handled in the same way. However, the column B data indicate that the distillation process results in the loss of urea. This result is qualitatively consistent with the effect of the preliminary distillation step used with the Kjeldahl urea analysis method.

The reason for the anomalous results with the audit sample number 4 is not evident. The fact that the audit sample 4 results are consistently higher than the actual concentration (even in column B) indicated the possibility of an initially erroneous sample weight or an error in the initial sample solution preparation.

These results above should be viewed as applicable only to urea solutions of high concentrations (on the order of 100,000 ppm). The extent of urea loss at <u>lower</u> concentrations is indicated by a comparison of the distilled and undistilled urea calibration curves used to analyze the August 1979 field samples. Two sets of standard urea solutions were prepared: the absorbances of one set were measured directly; the absorbances of the other set were measured after the standards were distilled. These data are shown in Table 2-19 and indicate an average decrease in absorbance of about 12 percent (distilled standards read 12% lower than undistilled).

TABLE 2-18

COMPARISON OF EPA AUDIT SAMPLES AND TRC UREA STANDARDS

		A		B		C	
		Distilled samples against distilled standards curve		Distilled samples against Direct standards curve		Direct samples against Direct standards curve	
Audit Sample Number	Actual Urea Concentration (ppm)	Indicated Concentration (ppm)	Percent Error*	Indicated Concentration (ppm)	Percent Error*	Indicated Concentration (ppm)	Percent Error*
1	265600	263000	-1.0	230000	-13.4	263000	-1.0
2	480000	459000	-4.4	402000	-16.3	455000	-5.2
3	419600	428000	2.0	371000	-11.6	408000	-2.8
4	99200	117000	17.9	103000	3.8	126000	27.0
5	199900	193000	-3.5	172000	-14.0	200000	0.1

*Percent error = (indicated - actual) * 100/actual.

Note: 1 ppm = 1 μg/ml

TABLE 2-19

DISTILLED AND UNDISTILLED UREA CALIBRATION CURVES
FOR THE P-DIMETHYLAMINOBENZALDEHYDE ANALYSIS METHOD

Urea Concentration (ppm)		Absorbance		
		Undistilled	Distilled	Decrease(%)*
0		0.000	0.000	--
125		0.186	0.162	-12.9
250		0.362	0.312	-13.8
375		0.526	0.461	-12.4
500		0.680	0.614	- 9.7
	Slope	0.00136	0.00122	
	Intercept	0.011	0.004	
	Corr. Coefficient	0.9993	0.9999	

*Decrease = (distilled - undistilled) * 100/undistilled.

2.5.2 Sulfuric Acid Interference

The sampling train used for these August 1979 emissions tests included impingers with 1N sulfuric acid (H_2SO_4). During the urea analyses of the first series of water and acid impinger samples (using the p-dimethylamino-benzaldehyde method with preliminary ammonia distillation), the TRC chemist noted that all the acid impinger samples read below the standard blank used to zero the spectrophotometer. Since the most obvious difference between the acid impinger samples, the water impinger samples, and the urea standards used to prepare the calibration curves was their acid content, the chemist reasoned that H_2SO_4 may be a negative interference:

acid impinger samples - 1N H_2SO_4

water impinger samples - 2 ml H_2SO_4/liter (preservative)

Calibration standards - No acid

To test this hypothesis, the chemist prepared four different water blanks and measured their absorbances (after zeroing the spectrophotometer on the first blank).

Blank	Absorbance
Water with preliminary NH_3 distillation	0.000
Dilute H_2SO_4 solution (2 ml/liter water) with preliminary NH_3 distillation	$\pm$0.004
1N H_2SO_4 with preliminary NH_3 distillation	-0.048
Water without preliminary NH_3 distillation	0.000

The absorbance of the dilute acid blank was slight (several measurements yielded absorbances in the range of $\pm$0.004). The 1N H_2SO_4 blank result was significant: an absorbance of 0.05 was equivalent to about 36 mg urea in a 1 liter sample. In order to compensate for this interference, urea

standards were subsequently prepared to contain the same acid concentration as the sample being analyzed.

In addition to emissions tests on prill tower scrubbers, tests were also performed on the urea solution synthesis tower vent during this program. The high ammonia content of the vent emissions required the use of 5N and 10N H_2SO_4 in the sample train impingers. Negative absorbances were also obtained with these samples, and the same procedure of urea standard solution acidification was followed to compensate.

The synthesis tower acid impinger samples exhibited turbidity when the PDAB color reagent was added. The turbidity was removed with the addition of 2 ml concentrated HCl to each sample. This turbidity problem was encountered during two other field programs conducted by TRC in April 1980.[1] On these programs, the turbidity was removed by adding 1 ml concentrated HCl to each sample.

2.6 Threshold Minimum Detectable Limit for the Proposed EPA Urea Analytical Method

The absolute threshold of detection (lowest urea concentration detectable in a spectrophotometer sample cell) for the p-dimethylaminobenzaldehyde (PDAB) analysis method was evaluated by TRC using laboratory urea solutions. In addition, during an emission testing program at a urea manufacturing facility, TRC investigated ways to improve the sensitivity of the PDAB analysis method so that samples with urea concentrations too low to normally measure can be readily analyzed.

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(1) Reichhold Chemicals, Inc., St. Helens Oregon; Union Oil Company, Brea, California. EPA Contract 68-02-2820, Work Assignments 19 and 20.

2.6.1 Laboratory Evaluation of the Absolute Urea Detection Threshold

EPA requested TRC to perform analyses of standard urea solution samples in order to estimate the minimum urea concentration detectable by the p-dimethylaminobenzaldehyde urea analysis method (with no preliminary distillation). Two sets of urea solutions were prepared: set 1 included five urea samples ranging from 50 ppm to 250 ppm; set 2 included seven urea samples ranging from 1 ppm to 30 ppm. Both sets were analyzed with a spectrophotometer using both a 1 cm sample cell and a 5 cm sample cell. The resulting four data sets were plotted on rectilinear graph paper as absorbance vs. urea concentration, and least-squares linear regression analyses were performed to determine best-fit line equations. These data are shown in Table 2-20 and Figures 2-2 through 2-5.

These data reflect the linear relationship between absorbance and concentration described by Beer's Law:[1]

$$A = kdC$$

where:
A = absorbance
k = absorptivity coefficient
d = path length (cell size)
C = concentration

The two 1-cm cell data sets yielded similar slopes. By applying the low concentration (set 2) absorbances to the high concentration (set 1) equation (rearranged to solve for concentration), the following concentrations were

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(1) Strobel, H.A., Chemical Instrumentation - A Systematic Approach to Instrument Analysis, Addison - Wesley, 1960, pp. 150 ff.

TABLE 2-20

DATA FROM UREA THRESHOLD OF DETECTION DETERMINATION

Concentration Group	Concentration (ppm)	Absorbance 1-cm Cell	Absorbance 5-cm Cell
Set 1	250	0.415	1.044
	200	0.332	0.984
	150	0.250	0.860
	100	0.157	0.618
	50	0.087	0.368
	0	0	0
Set 2	30	0.051	0.223
	20	0.033	0.132
	10	0.015	0.067
	7	0.010	0.048
	5	0.003	0.013
	2	0.000	0.003
	1	-0.007	---*
	0	0	0

* Indefinite, but less than zero.
Not used as a data point.

Least-Squares Linear Regression Analyses of Above Data

Absorbance = M * Concentration + Y

	1-cm Cell			5-cm Cell		
	M	Y	R**	M	Y	R**
Set 1	0.00166	-0.0005	0.9996	0.00418	0.1235	0.9685
Set 2	0.00185	-0.0042	0.9914	0.00757	-0.0106	0.9941

** Correlation Coefficient

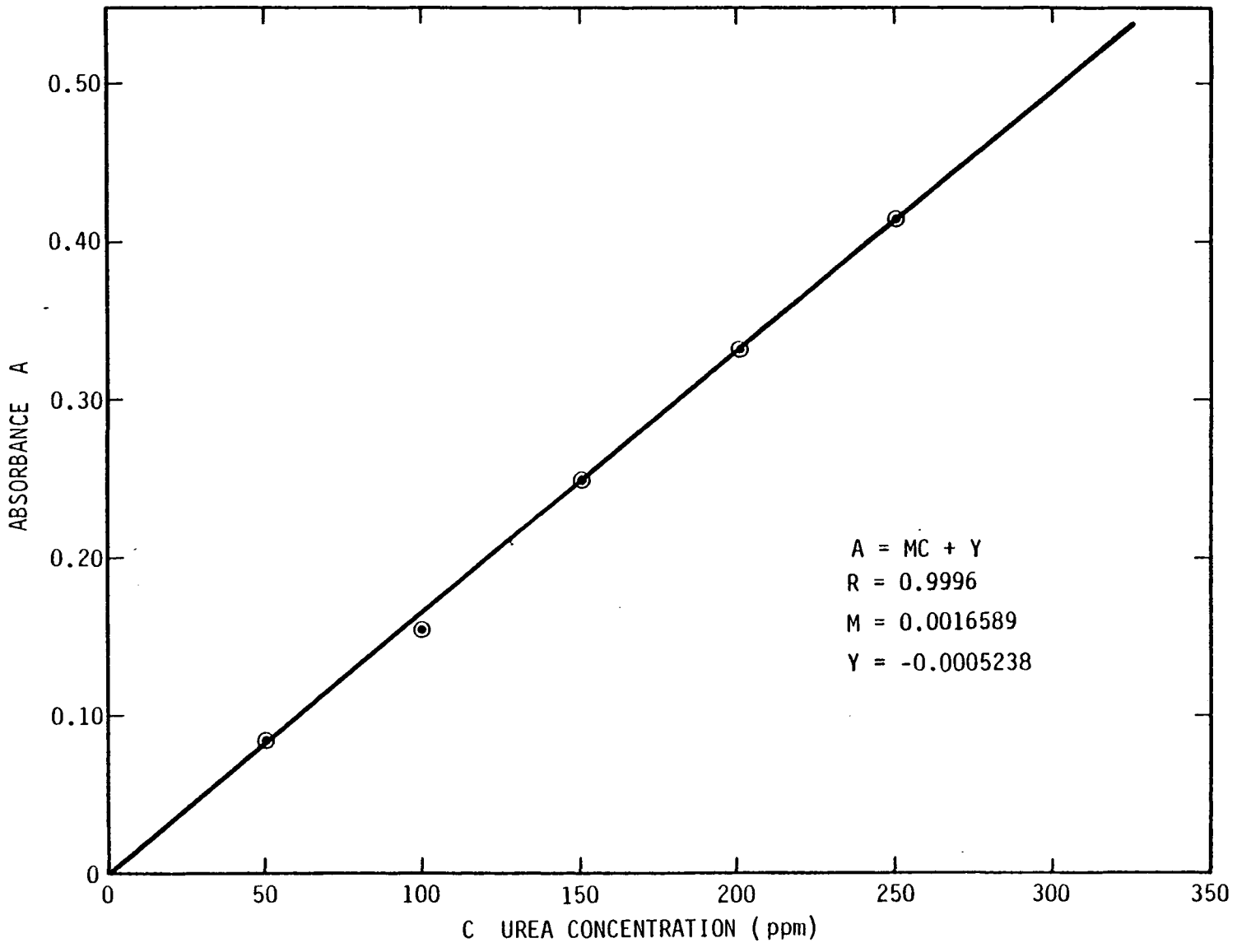


FIGURE 2-2: UREA THRESHOLD OF DETECTION DETERMINATION
SET 1 1 cm CELL

0988-003

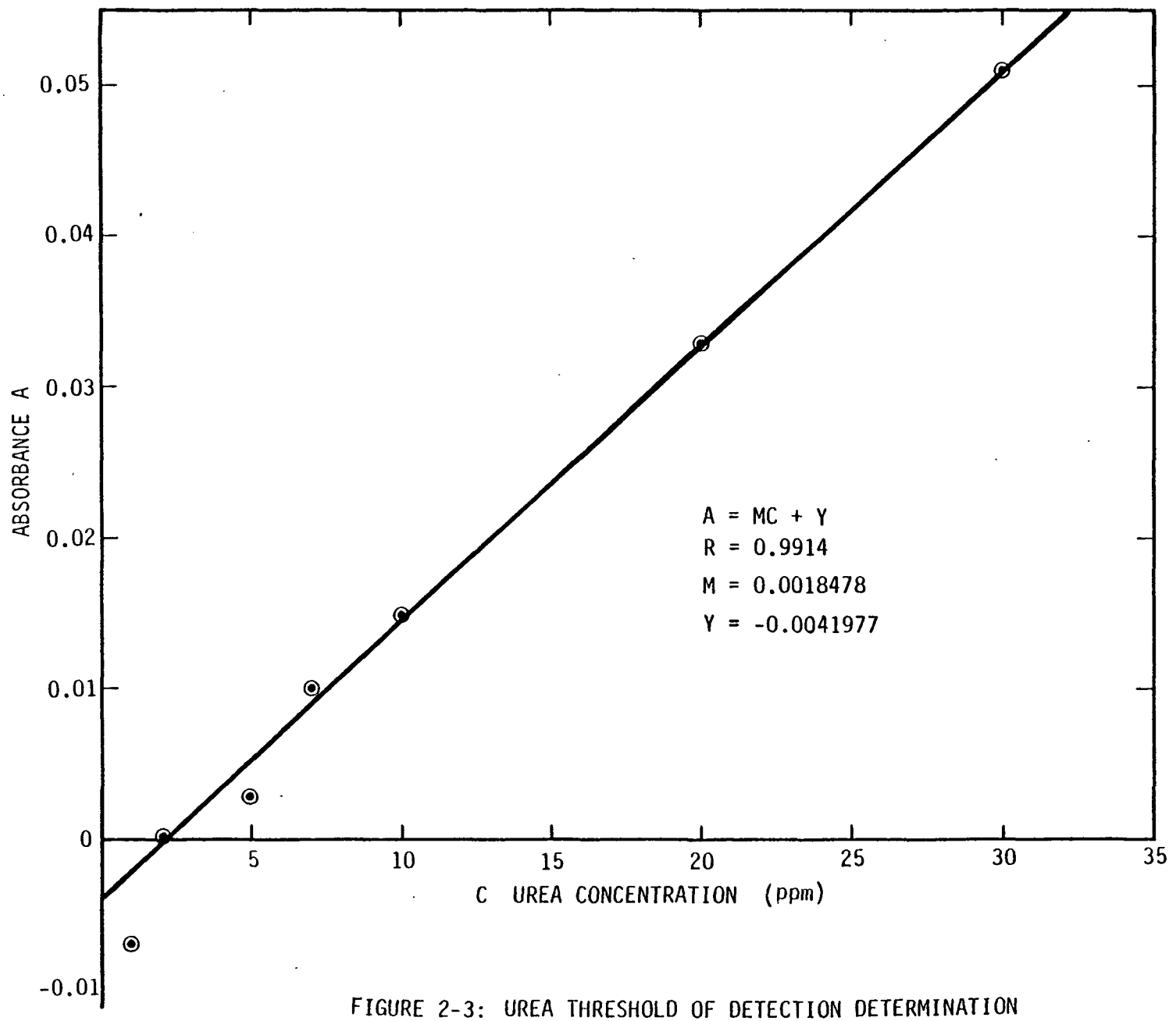
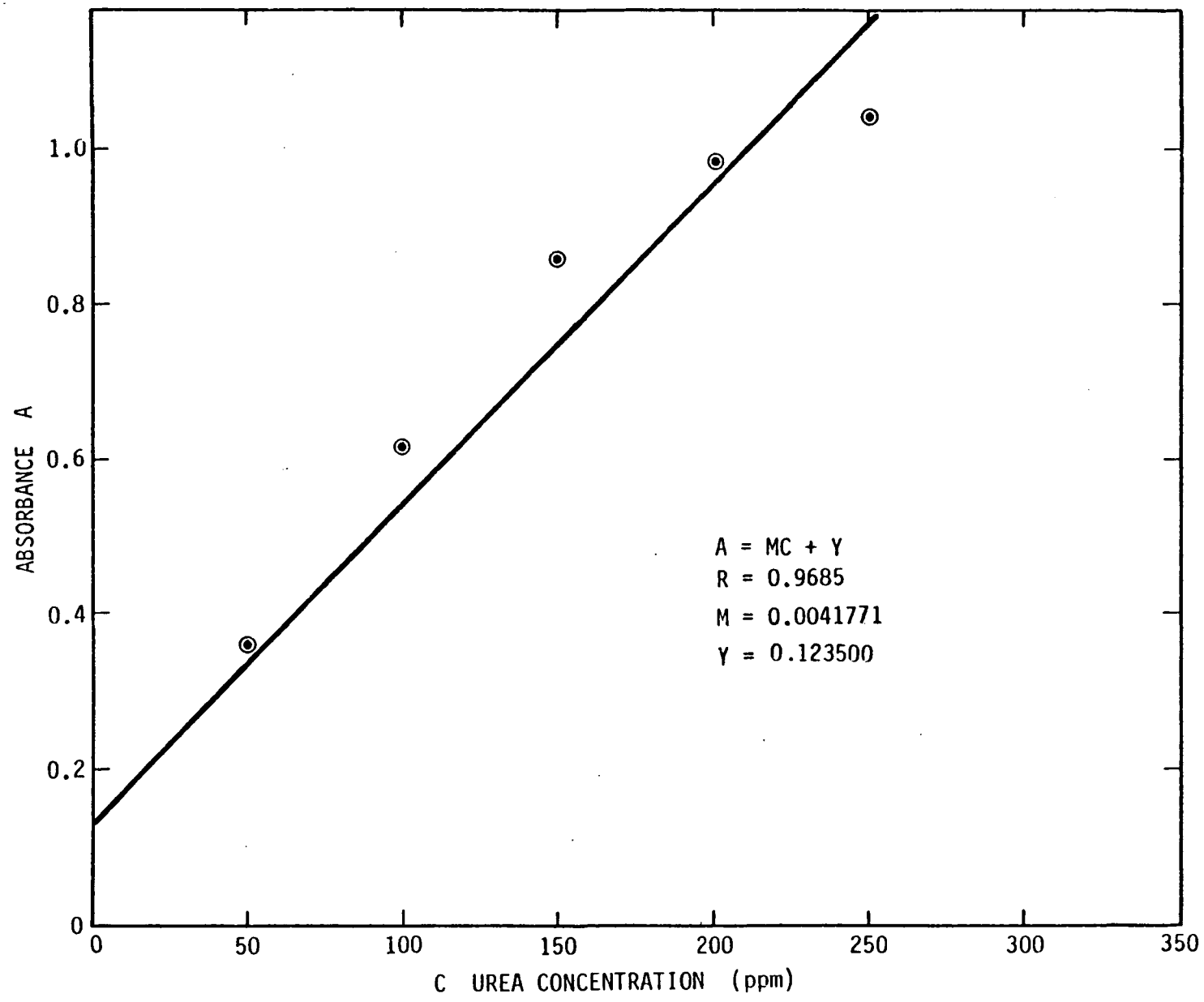


FIGURE 2-3: UREA THRESHOLD OF DETECTION DETERMINATION
SET 2 1 cm CELL

0988-004



0988-005

FIGURE 2-4: UREA TRESHOLD OF DETECTION DETERMINATION
SET 1 5 cm CELL

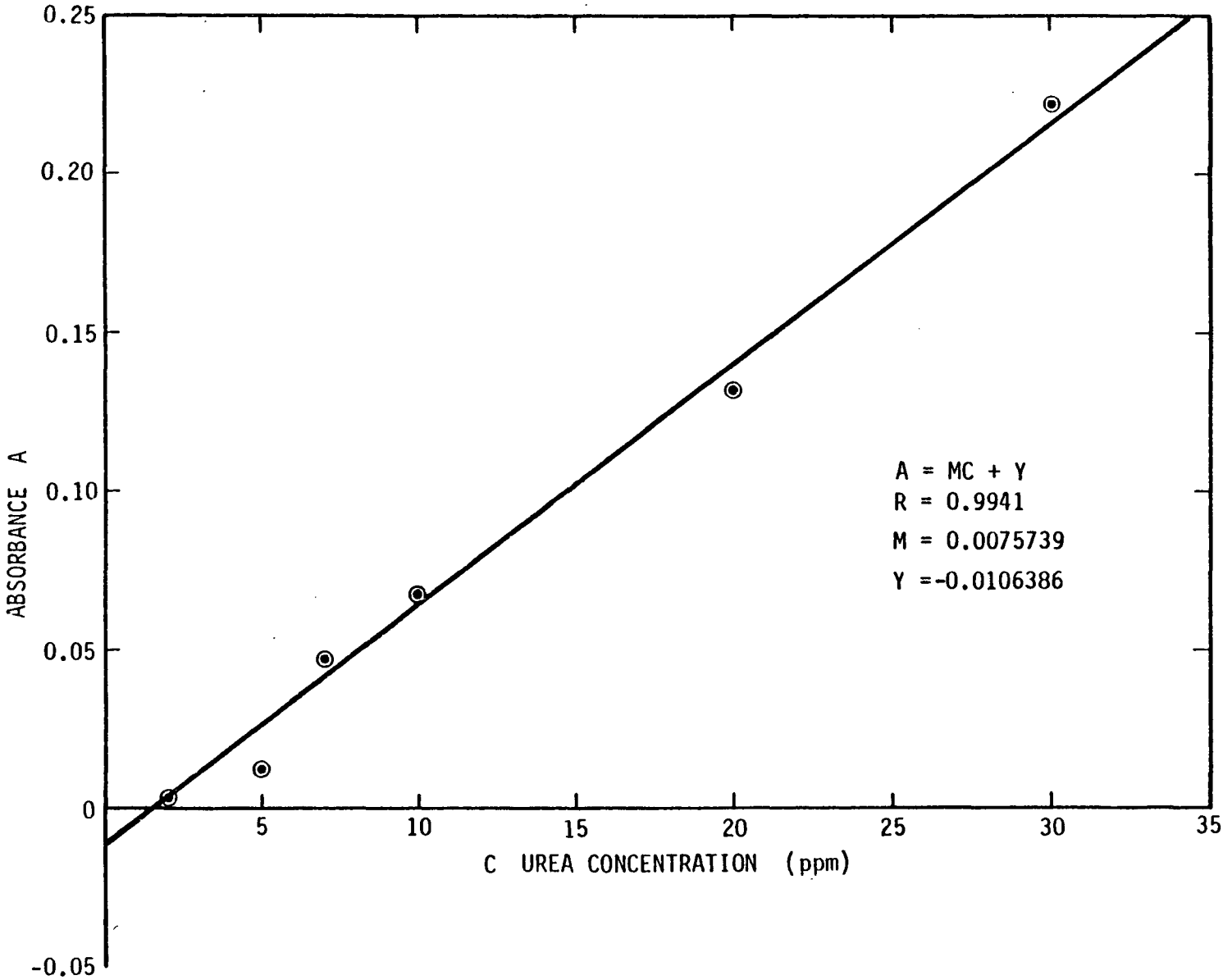


FIGURE 2-5: UREA THRESHOLD OF DETECTION DETERMINATION
SET 2 5 cm CELL

0988-006

calculated:

Low Concentrations Calculated By High Concentrations Equation (ppm)	Actual Low Concentrations (ppm)
31.1	30.0
20.2	20.0
9.4	10.0
6.3	7.0
2.1	5.0
0.3	2.0
-3.9	1.0

One may infer from these results that the sensitivity of this urea analysis method fails at about 7 ppm and that the threshold of the method is at this point. Further consideration of these 1-cm cell data and the 5-cm cell data can, however, yield more refinement in the estimated detection threshold, as follows.

The 5-cm cell data show slopes more positive than the 1-cm cell data, as predicted by Beer's Law. The apparent bending over of the 5-cm set 1 curve above 150 ppm (Figure 2-4) may be evidence of a fundamental constraint on Beer's Law, namely that the law is applicable primarily in dilute solutions (less than 0.02 M).[1] For urea in a 5-cm cell, the upper limit may in fact be considerably less than 0.02 M (1200 ppm). This deviation from linearity results in the considerable difference between the slopes of the 5-cm set 1 and set 2 equations.

Both set 2 data groups (1-cm cell and 5-cm cell) indicate considerably better resolution at very low concentrations than do the set 1 (high concentration) data, as would be expected. Concentrations as low as 3-5 ppm could

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(1) Ibid.

be read with a fair degree of confidence from Figures 2-3 and 2-5, with the 5-cm cell data providing even slightly more accuracy than the 1-cm cell data. (The integrating effect of the larger path length would naturally provide better resolution at low concentrations.)

Extrapolating relatively high concentration calibration curves down to read low concentrations is not advisable in most analytical situations. The best approach is to prepare a curve that covers the concentration range of interest. The advantage of this technique is evident in Figures 2-3 through 2-5. Also evident is the utility of using a 5-cm cell over a 1-cm cell in order to obtain better resolution at low urea concentrations. At high urea concentrations a 1-cm cell would be preferred.

The continuity of both the 1-cm cell data and the 5-cm cell data is clearly shown in Figure 2-6, where the absorbance vs. concentration data are plotted on log-linear graph paper. This figure also illustrates the points discussed above:

- The separation of the two curves reflecting the slope change that occurs when the path length is changed.
- The slightly increased resolution of the 5-cm cell data at low concentrations.
- The saturation apparent in the 5-cm cell at high concentrations.

2.6.2 Low Level Urea Analysis in the Field

During an emissions testing program[1] at a urea manufacturing facility in April 1980, TRC modified some steps in the PDAB urea analysis method (with

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(1) EPA Report 80-NHF-14, "Process Emissions Testing at the Reichhold Chemicals, Inc., Urea Manufacturing Facility, St. Helens, Oregon". Prepared by TRC under EPA Contract 68-02-2820, Work Assignment 19.

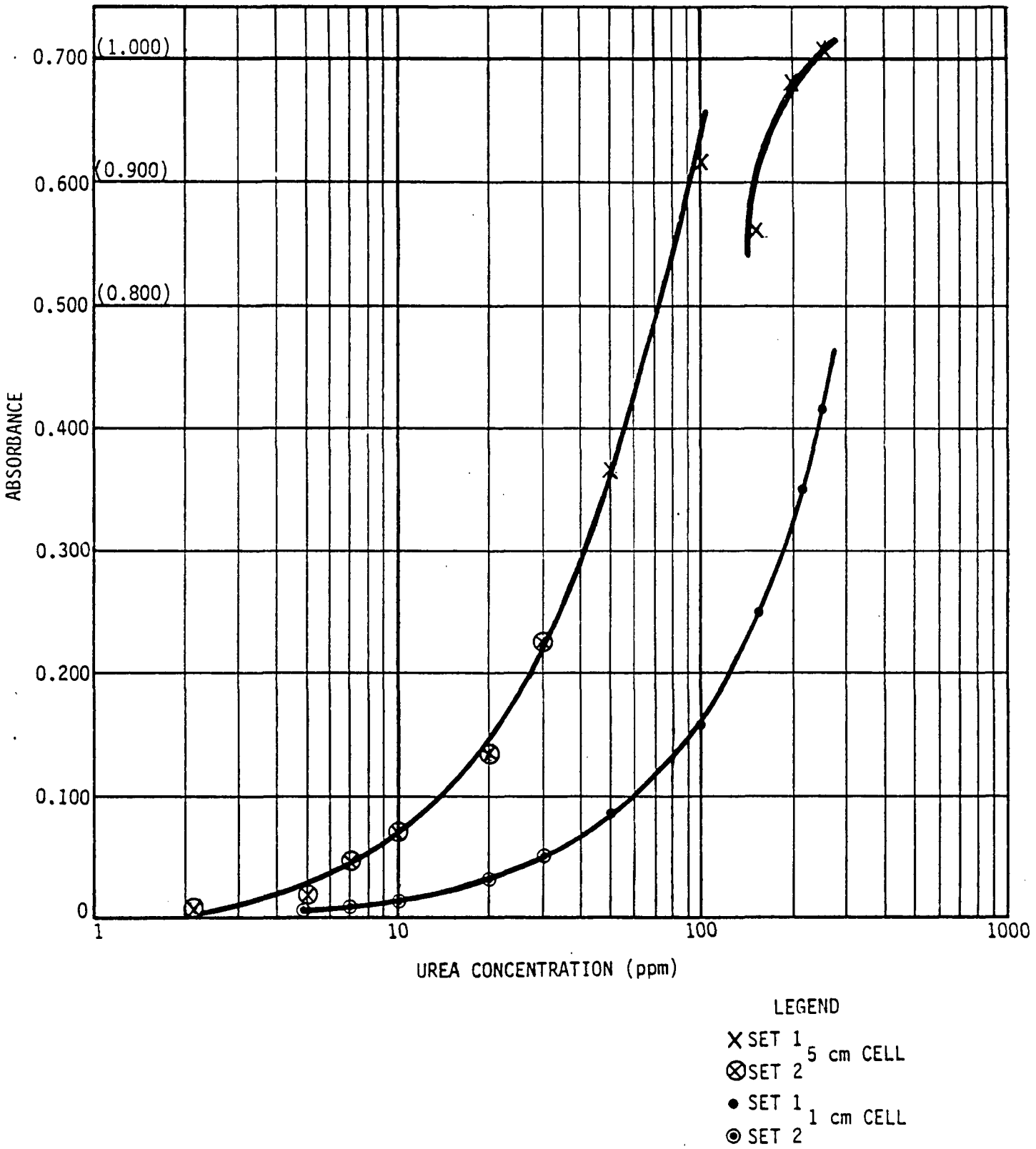

FIGURE 2-6: UREA THRESHOLD OF DETECTION DETERMINATION

0988-002

preliminary distillation) in order to analyze very low urea concentrations in the impinger samples. Low urea emissions were expected at this facility, but even with extended sampling times (up to 500 minutes per test run), urea concentrations in the sampling train impingers were near the threshold of detection (using the PDAB analysis method as written).

The method was modified by increasing the size of the sample aliquot used for analysis from 100 ml up to 700 ml and boiling this larger volume down to 100 ml (to remove ammonia). In this way, the amount of urea available for final analysis was increased by up to a factor of seven, and the sample absorbances were brought into the working range of the calibration curve.

2.7 Collection Efficiency Determination of the EPA Urea Sampling Train

Three emission test runs were performed by TRC on April 24, 1980 on the outlet of a prill tower scrubber.[1] One purpose of these tests was to provide information on the urea collection efficiency of the modified EPA particulate sampling train.

The impinger sequence used for these tests was as follows:

impingers 1 and 2	-	deionized, distilled water
impingers 3 and 4	-	1N sulfuric acid
impinger 5	-	empty
impinger 6	-	silica gel

The probe wash, the contents of impinger 1, the contents of impinger 2, and the combined contents of impingers 3, 4, and 5 were analyzed individually for

(1) EPA Report 80-NHF-15, "Process Emissions Tests at the Union Oil Company Urea Manufacturing Facility, Brea, California". Prepared by TRC under EPA Contract No. 68-02-2820, Work Assignment No. 20.

urea and ammonia at the TRC laboratories within 20 days of sample collection. Urea analysis was performed using the p-dimethylaminobenzaldehyde method with preliminary distillation. Ammonia analysis was performed using the specific ion electrode method.

The analysis results for these three prill tower scrubber test runs are shown in Table 2-21. These data indicate that 70% of the urea in the sampled gas is retained by the first water impinger (and probe), and the remaining urea is all retained by the second water impinger. The ammonia data indicate that half the ammonia is retained by the water impingers and half by the acid impingers. To determine whether any significant amount of ammonia gets by even the acid impingers would require other tests using additional impingers.

As mentioned in Section 2.5.2, the acid impinger samples exhibited turbidity when the PDAB color reagent was added. This turbidity was removed when 1 ml of concentrated HCl was added to each sample.

2.8 Conclusions and Recommendations

The following conclusions are based on the urea analysis method investigation results and supplemental discussions presented in Sections 2.0 and 3.0 of this report.

1. Of the two urea analysis methods evaluated (the p-dimethylaminobenzaldehyde (PDAB) method and the Kjeldahl method), the PDAB method is preferred because it is simpler to use and measures urea directly.

2. The absolute threshold of detection for the PDAB method is 5-7 ppm. Urea concentrations lower than this in impinger samples can be readily determined by concentrating the urea sample prior to analysis. This concentration step involves a slight modification to the proposed EPA Reference Method procedure.

3. The interfering effects of ammonia on the PDAB method as discussed by Watt and Chrisp in 1954 are generally corroborated by the effects determined by TRC, described herein. The TRC results show a slight (less than 2%) interference for a 20:1 ammonia to urea molar ratio. Higher molar ratios increase the interference.

TABLE 2-21

UREA SAMPLING TRAIN COLLECTION EFFICIENCY RESULTS
UNION OIL COMPANY, BREA, CALIFORNIA

	Test Run		Probe Wash	Impinger 1	Impinger 2	Impingers 3,4,5	Total
Urea	1	milligrams	4.50	44.6	28.8	<1.64*	77.90
		percent	5.8	57.3	36.9	0	100
	2	milligrams	4.83	31.8	13.5	<1.58*	50.13
		percent	9.6	63.4	27.0	0	100
	3	milligrams	5.58	41.1	15.3	<1.49*	61.98
		percent	9.0	66.3	24.7	0	100
	Average	milligrams	4.97	39.2	19.2	-	63.34
		percent	7.8	61.9	30.3	0	100
Ammonia	1	milligrams	5.43	72.6	26.9	67.5	172.43
		percent	3.1	42.1	15.6	39.2	100
	2	milligrams	2.83	50.1	40.1	102	195.03
		percent	1.5	25.7	20.6	52.2	100
	3	milligrams	3.10	110	63.3	199	375.40
		percent	0.8	29.3	16.9	53.0	100
	Average	milligrams	3.79	77.6	43.4	123	247.62
		percent	1.5	31.3	17.5	49.7	100

* Detection Threshold (0.010 absorbance reading). Urea standards were prepared with similar acid contents as these acid impinger samples.

4. The extent of urea loss during preliminary distillation to remove ammonia prior to PDAB analysis appears to be 12 to 14 percent, based on analyses of samples with urea concentrations in the ranges of 0-500 ppm and 100,000-500,000 ppm.

5. Sulfuric acid is a negative interference in the PDAB urea analysis method. For this reason, the sulfuric acid content of samples and standards should be the same.

6. The urea content of field and laboratory samples undergoes no detectable deterioration over time, up to 21 days after sample collection/preparation. Mercuric chloride and sulfuric acid have no discernable effect as urea stabilizing agents.

7. Nearly 100% of all sampled urea appears to be caught in the first two (water) impingers of the EPA urea sampling train.

3.0 DISCUSSION OF ANALYSIS PROCEDURES

This section presents more detailed descriptions of the analysis procedures used in the investigations presented in Section 2.0. The EPA report 79-NHF-13a[1] fully describes the December 1978 Agrico Chemical Company emissions testing program, and details of the Agrico data presented in Sections 2.1 and 2.2 are not included in this section.

3.1 Preservation Analyses

The scrubber outlet gas stream samples obtained during the emissions testing program at the Agrico Chemical Company in December 1978, and prepared laboratory urea samples were treated with two preservative reagents in order to assess the stabilizing effects of these reagents on the urea and ammonia content of the samples. Mercuric chloride and sulfuric acid were added to the samples which were then analyzed over a 15-20 day time period in December 1978 and January 1979.

3.1.1 Field Sample Preservation Analyses

The six scrubber outlet gas stream samples were initially analyzed for urea and ammonia at the Agrico laboratory within 24 hours of sample collection. The samples were then treated with preservative and returned to TRC for the preservation analyses. A white precipitate formed in the mercuric chloride preserved samples. The nature of this precipitate is unknown, but during subsequent analyses at TRC these samples were agitated to include this precipitate in the analyzed aliquot.

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(1) EPA Report 79-NHF-13a, "Process Emissions Tests at the Agrico Chemical Company Urea Manufacturing Facility, Blytheville, Arkansas". Prepared by TRC under EPA Contract No. 68-02-2820, Work Assignment No. 11.

The preservation procedure consisted of separating each sample into two equal portions. To one portion was added saturated mercuric chloride (approximately 2 ml/liter of sample); to the other portion was added concentrated sulfuric acid (approximately 2 ml/liter of sample). The samples then remained at room temperature and were analyzed for urea and ammonia, starting 6-8 days after the initial analyses and then every 2-4 days for about a 2 week period. The urea analyses were performed with the Kjeldahl method, with preliminary distillation and finishing with nesslerization. The ammonia analyses were performed by direct nesslerization and by nesslerization with preliminary distillation.

The preliminary distillation was a step common to the Kjeldahl urea and distillation/nesslerization ammonia analyses. Sodium borate and sodium hydroxide were added to a portion of the sample to act as a buffer and to bring the pH to 9.5 or greater. The sample was then distilled, and the distillate (containing the ammonia) was collected in a boric acid solution. To this solution was added the nessler reagent, and after full color development the absorbance of this solution was measured with a spectrophotometer. To the distillation residue was added the Kjeldahl digestion reagent which converts organic nitrogen (urea) to ammonia. This converted ammonia was then distilled into an acid solution and analyzed by nesslerization as above.

Sample absorbance measurements were converted to ammonia concentration through a calibration curve prepared with a series of standard ammonia solutions. Urea concentrations were calculated by multiplying the organic nitrogen ammonia concentrations by the stoichiometric factor 60/34.

Direct nesslerization ammonia measurements were made by adding the nessler reagent directly to a portion of the sample, awaiting full color development,

and taking the absorbance reading with the spectrophotometer. A separate calibration curve was prepared for the direct nesslerization measurements.

One complication of the preliminary distillation step to remove ammonia is the hydrolysis of urea to ammonia that occurs during the distillation. It has been estimated that about 7 percent of the urea in a sample is converted to ammonia during the preliminary distillation step. Therefore, the indicated urea concentration multiplied by 1.07 equals the actual urea concentration. At the same time, the indicated ammonia concentration must be reduced by a stoichiometrically equivalent amount. Since 2 moles (34 grams) of ammonia are formed from the hydrolysis of 1 mole (60 grams) of urea, the ammonia correction equation is as follows:

$$Aa = Ai - (Ua * 0.07 * 34/60)$$

Where Aa = actual ammonia concentration

Ai = indicated ammonia concentration

Ua = actual urea concentration

If the actual urea concentration is small relative to the ammonia concentration, then these corrections are insignificant. However, if the urea concentrations are large (as, for example, in scrubber liquor streams) compared to ammonia concentrations, then the ammonia corrections are unrealistic, resulting in negative actual ammonia concentrations.

The direct nesslerization analysis and the preliminary distillation step were often performed on one day and the subsequent nesslerization and Kjeldahl analyses performed one or several days later. In these cases, the date of analysis was defined as the day that the preliminary distillation was performed.

During the urea analyses of the scrubber outlet gas stream samples, an absorbance reading was occassionally higher than the color intensity would

normally indicate. This occurred with blanks also. In these cases when the absorbance appeared to be too high, the samples were visually compared to standards. Since these gas stream samples contained relatively low urea concentrations, high blank corrections were significant when they occurred. (See Appendix C for a breakdown of each sample analysis.) This effect was probably due to a reagent since it occurred in both blanks and samples.

3.1.2 Laboratory Sample Preservation Analyses

When the field sample preservation analyses were completed, the following series of laboratory urea solutions were prepared at TRC with distilled, deionized water:

A: 40 mg urea per liter of water
B: 100 mg urea per liter of water
C: 40 mg urea per liter of water with 2 ml saturated mercuric chloride
D: 100 mg urea per liter of water with 5 ml saturated mercuric chloride
E: 40 mg urea per liter of water with 2 ml concentrated sulfuric acid
F: 100 mg urea per liter of water with 5 ml concentrated sulfuric acid

Blank M: 5 ml saturated mercuric chloride per liter of water
Blank A: 5 ml concentrated sulfuric acid per liter of water

The preservation reagents were added to the urea and blank solutions before they were diluted to volume. These solutions remained at room temperature for 19 days and were analyzed for urea and ammonia every 2-3 days during that time, for a total of 9 analyses. The initial analysis was done the same day that the samples were prepared. The analyses were performed in the same manner and with the same methods as the field samples, as described in Section 3.1.1. above.

The blanks in some cases yielded absorbances that appeared high when compared to standards, presumably due to a reagent, as mentioned in Section 3.1.1. A breakdown of each sample analysis is shown in Appendix C.

3.2 Ammonia Interference on Urea Analysis

The interfering effects of ammonia on the p-dimethylaminobenzaldehyde (PDAB) urea analysis method (with no preliminary distillation) were investigated by TRC in March 1979 under technical directive No. 2 of EPA Work Assignment 11. Four urea standard solutions (50, 100, 150, and 200 ppm) and a blank were analyzed by adding the PDAB reagent, waiting for full color development, and measuring the absorbance of each solution in a spectrophotometer. A calibration curve of absorbance vs. urea concentration was then drawn. Five additional solutions were then prepared, each containing 100 ppm urea and 100, 500, 1000, 5000, and 10000 ppm ammonia, respectively. The ammonia was added from a standard solution of ammonium chloride (NH_4Cl). To each of these five solutions was added the PDAB reagent, and the absorbance of each was measured and converted to urea concentration with the prepared calibration curve.

The results, as discussed in Section 2.4, indicate that ammonia is a noticeable positive interference (indicating higher urea concentrations than actually exist) when the mole ratio of urea/ammonia exceeds approximately three. At a mole ratio of 3.5, a 1% error was measured. These analyses were performed with 100 ppm urea solutions, and may not necessarily apply to all urea concentrations. The relationship between the urea/ammonia mole ratio and the indicated error may change with the absolute urea concentration.

3.3 Evaluation of Standard Procedures for the Proposed EPA Urea Analytical Method

Two procedural aspects of the p-dimethylaminobenzaldehyde (PDAB) urea analysis method were investigated by TRC during an emissions test program at a urea manufacturing facility in August 1979. These aspects were: preliminary distillation (to remove ammonia) and sulfuric acid as an interference.

3.3.1 Effects of Preliminary Distillation

As is shown in Sections 2.4, ammonia can interfere with the analysis of urea by the PDAB method. Ammonia can be removed by first distilling (boiling) a sample; the effects of this distillation on the urea content of the sample were investigated and the results of this investigation are discussed in Section 2.5.

The method of investigation centered on the analysis by TRC of five urea-in-mannitol audit samples that were prepared by EPA. These samples were each dissolved in 100 ml of distilled, deionized water, and these audit sample solutions were then divided into two portions. A sodium borate buffer and sodium hydroxide were added to the first portions to bring the pH to 9.5 or greater; these portions were then distilled (boiled) to remove ammonia. To the residues were added the PDAB reagent and the absorbances of these solutions were measured in a spectrophotometer. The second portions remained undistilled and their absorbances were measured after the addition of the PDAB reagent.

The absorbances of distilled and undistilled standard urea solutions were also measured, and a distilled calibration curve and an undistilled calibration curve were prepared by plotting absorbances vs. urea concentration. The audit sample absorbances (distilled and undistilled) were then read against both distilled and undistilled standard calibration curves.

The results, as discussed in Section 2.5, show that the preliminary distillation step, while removing ammonia, also apparently removes some urea. Hydrolysis of some urea to ammonia may be occurring (as in the Kjeldahl preliminary distillation step) and this converted urea is boiled off along with any original ammonia. The degree of urea removal appears to be about 14 percent.

An effect of the ammonia-removing preliminary distillation step is an apparent decrease in the sensitivity of the PDAB method. This decrease in sensitivity is, however, only apparent. As discussed above, distillation results in a loss of urea. This loss is reflected in a decrease in the intensity of color development and, therefore, a decrease in absorbance. The data for the distilled and undistilled standard calibration curves used for the August 1979 field sample analyses, shown in Table 2-19, illustrate this. The average decrease in absorbance (averaged over the four urea concentrations used) is about 12.2 percent. This implies that the distilled absorbances reflect not the indicated urea concentrations but urea concentrations 12 percent lower, and that the distilled calibration curves should be a plot of distilled absorbance vs. decreased urea concentrations. Further investigations are needed to better define the extent of urea loss during distillation.

3.3.2 Sulfuric Acid Interference

The water impinger samples from this August 1979 emissions test program were preserved with 2 ml sulfuric acid (H_2SO_4) per liter of sample. The acid impingers used at the prill tower scrubber contained 1N H_2SO_4, and the acid impingers used at the synthesis tower vent contained 5N and 10N H_2SO_4. The water and acid impinger samples were analyzed for urea with the PDAB method with preliminary distillation. Immediately prior to distillation, the pH of the samples was brought to greater than 9.5 with the addition of sodium hydroxide (1N NaOH added to the water samples and 10N added to the acid samples).

In the analysis of the first test run samples, the absorbances of the acid impinger samples were less than the absorbance of the blank used to zero the spectrophotometer; one of these samples read about -0.040 absorbance units.

To test whether H_2SO_4 was interfering, four different water blanks were prepared and their absorbances were measured, as described in Section 2.5. The two straight water blanks (one distilled, the other undistilled) both read zero. The absorbance of the dilute acid blank (2 ml H_2SO_4/ liter) ranged between ± 0.004, and the absorbance of the strong acid blank (1N H_2SO_4) was -0.048. This result appeared to confirm the fact that the H_2SO_4 did negatively interfere with the urea analysis, and subsequently urea standards were prepared containing the same amount of acid as the samples. Water impinger samples and acid impinger samples were, therefore, analyzed separately.

The synthesis tower sample analyses were more complex than the prill tower scrubber analyses. The acid impingers used in synthesis tower tests 1 and 2 contained 10N H_2SO_4, and the impingers in test 3 contained 5N H_2SO_4. For all three tests the impingers were washed with 1N H_2SO_4. Thus, two different H_2SO_4 concentrations resulted when impinger contents and washes were combined. Since the volumes of each acid used were known, the normality of each combined samples was calculated: samples 1 and 2 averaged 6.0N; sample 3 was 3.7N.

The synthesis tower acid impinger samples and standards required 40 to 60 ml of 10N NaOH per 100 ml aliquot in order to adjust the pH to 9.5 for the preliminary ammonia removal. It was impossible to boil down the samples to less than 100 ml without severe "bumping" due to the high concentration of dissolved solids. Therefore, these samples and standards were diluted to 200 ml. This decreased the sensitivity of this method by a factor of 2 for these three samples.

A 10 ml aliquot of the 200 ml dilution was added to a 25 ml volumetric flask and 10 ml of the PDAB color reagent was added. All samples and standards then formed a precipitate which caused turbidity. With the addition of 2.0 ml concentrated HCl to each the precipitate completely dissolved in the 3.7N H_2SO_4 solutions and almost completely in the 6.0N H_2SO_4 solutions. However, the absorbances of the three test samples remained below zero:

Synthesis Tower Test No.	Absorbance
1	<-0.010
2	-0.004
3	-0.009

When the test 1 sample was read against a blank containing the exact H_2SO_4 normality (5.8N) of test sample 1 (after the spectrophotometer was zeroed on this blank), the sample still read -0.007.

These synthesis tower data were interpreted to mean that the synthesis tower urea concentrations were less than the detection threshold of the analysis method. Further investigations on the effects of H_2SO_4 on the PDAB method are warranted.

The turbidity (mentioned above) that occurred with the addition of the PDAB color reagent to the acid and NaOH treated samples was encountered during two urea prill tower emissions test programs conducted by TRC in April 1980.[1] During these programs, when the color reagent was added to the treated samples and standards (after preliminary distillation), the solutions turned cloudy. This turbidity was removed with the addition of 1.0 ml

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(1) Reichhold Chemicals, Inc., St. Helens, Oregon; Union Oil Company, Brea, California. EPA contract 68-02-2820, Work Assignments 19 and 20.

concentrated hydrochloric acid. The turbidity was probably caused by an excess amount of NaOH added for ammonia removal. The subsequent absorbance readings were consistent with the visual color development.

3.4 Threshold Minimum Detectable Limit for the Proposed EPA Urea Analytical Method

3.4.1 Laboratory Evaluation of the Urea Detection Threshold

The absolute urea detection threshold of the p-dimethylaminobenzaldehyde (PDAB) analysis method was evaluated by TRC in March 1980. Two sets of standard urea solutions were used: set 1 included five solutions ranging from 50 ppm to 250 ppm (high concentrations); set 2 included seven solutions ranging from 1 ppm to 30 ppm (low concentrations). PDAB color reagent was added directly to these solutions (without preliminary distillation) and the solution absorbances were measured in a spectrophotometer using both a 1 cm sample cell and a 5 cm sample cell. Four calibration curves were prepared by plotting absorbance vs. urea concentration for both solution sets and both sample cells.

As discussed in Section 2.6.1, the slopes of the set 1 and set 2 calibration curves were similar for the 1 cm cell data. This allows for accurate low concentration analyses, down to about 7 ppm; the threshold of the method, using a high concentration calibration curve, is then about 7 ppm.

The 5 cm cell slopes of the set 1 and set 2 calibration curve differed, primarily due to the non-linearity of the high concentration curve. This non-linearity is apparently the result of saturation within the 5 cm cell at the highest concentrations. It does appear, however, that the 5 cm cell will allow for slightly lower absolute concentration measurement (lower than what could be obtained from a 1 cm cell) because of the integrating effect of the larger path length.

3.4.2 Low Level Urea Analysis in the Field

The proposed urea analysis EPA Reference Method 28 (PDAB) was used for the analysis of prill tower scrubber outlet samples during an April 1980 emissions testing program.[1] Both samples and urea standards were treated for ammonia removal by adding sodium borate buffer and sodium hydroxide and boiling. Urea analysis was then performed by adding PDAB color reagent and measuring absorbance in a spectrophotometer.

The lowest practical absorbance reading with the spectrophotometer is about 0.010 absorbance units; this was equivalent to about 10.4 ppm, based on an average from the eight urea calibration curves used for the analysis of the field samples. The calibration curves were prepared in accordance with the proposed EPA PDAB reference method (contained in Appendix A).

It was known beforehand that the controlled urea emissions from this prill tower scrubber would be extremely low. Consequently, the sampling time for each test run at the outlet was planned to be unusually long (320 minutes). Even with this long sampling time, the analysis of the first samples resulted in urea concentrations near the threshold of detection. It was decided that the sampling time should be lengthened to 500 minutes, and that the analysis procedure should be modified to be able to accurately measure the low urea sample contents.

The PDAB method presently calls for a 100 ml aliquot of sample to be boiled to remove ammonia and then be diluted back up to 100 ml; the color reagent is then added to a 10 ml portion of this solution. In order to increase the amount of urea in the spectrophotometer sample cell, larger

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(1) Reichhold Chemicals, Inc., St. Helens, Oregon.

sample aliquots were taken (up to 700 ml) and boiled down to 100 ml. A 10 ml portion of this solution now contained up to 7 times as much urea as the 10 ml portion prepared under the originally followed procedure. And the sample absorbances were brought into the working range of the calibration curve.

The total water impinger sample volumes for the six scrubber outlet test runs performed on this program were as fol ows:

Run No.	Water Impinger Sample Volume (ml)
1	1073
2	1175
3	1220
4	1180
5	1140
6	1060
Average	1141

Sufficient sample volume remained after the initial aliquot was drawn so that a repeat analysis could be performed if necessary.

By using this urea concentrating procedure, the effective threshold of detection of the method (the minimum urea concentration in the sampling train impingers that is detectible) was lowered by up to a factor of seven (from 10.4 ppm to 1.5 ppm). The minimum detectable urea concentration in a spectrophotometer sample cell (absolute threshold of detection) remained unchanged, of course.

Whatever can be done to increase the urea concentration in the impingers will help increase the sensitivity of the analysis method without the need to concentrate sample aliquots. Factors involved here are the sampling time and wash volumes. When urea concentrating is needed, the best sensitivity is obtained by concentrating the largest possible sample aliquot. Enough sample may need to be retained, however, in order to do repeat analyses or analyses for different parameters.

3.5 Collection Efficiency Determination of EPA Urea Sampling Train

Three 144-minute emissions tests were performed by TRC on the outlet of the northeast scrubber atop the prill tower at the Union Oil Company urea manufacturing plant in Brea, California, on April 24, 1980. This sampling was performed with a modified EPA sampling train and the contents of the sampling train impingers were analyzed in a manner to evaluate the urea collection efficiency of the train. A brief description of the sampling and analysis methods used for these tests is presented in this section. Complete details of this sampling program are contained in EPA report 80-NHF-15.[1]

3.5.1 Sampling Methods

The sampling train used is shown in Figure 3-1, and is a modification of the standard EPA Reference Method 5 sampling train. The sampling train consists of a nozzle, probe, teflon line, six impingers, vacumm pump, dry gas meter, and an orifice flow meter. The nozzle is stainless steel and is of a buttonhook shape. It was connected to a 5/8" stainless steel glass lined probe. Following the probe, the gas stream passed through a 3/8" I.D. Teflon line into an ice bath/impinger system.

The first two impingers each contained 100 ml of deionized distilled water. The next two impingers were filled with 1N H_2SO_4 (100 ml each). The fifth impinger remained empty while the sixth was filled with 200 grams of indicating silica gel to remove any remaining moisture.

3.5.2 Sample Recovery and Preparation

At the completion of each test run, the train was leak checked. Then the

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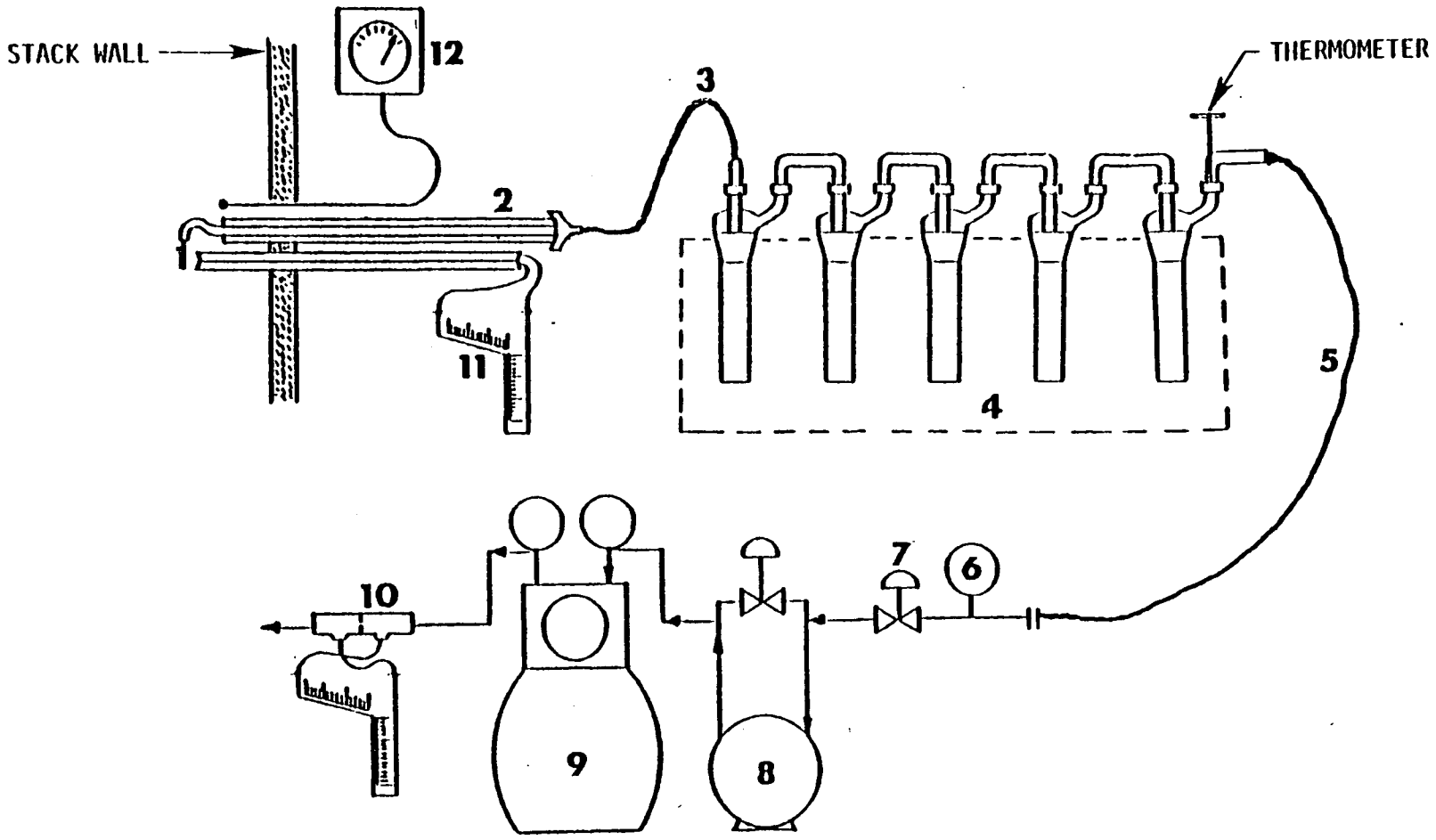
(1) EPA Report 80-NHF-15, "Process Emissions Tests at the Union Oil Company Urea Manufacturing Facility, Brea, California". Prepared by TRC under EPA Contract No. 68-02-2820, Work Assignment No. 20.



LEGEND

1 - NOZZLE	7 - NEEDLE VALVE
2 - PROBE	8 - PUMP
3 - TEFLON LINE	9 - DRY GAS METER
4 - ICE BATH	10 - ORIFICE
5 - FLEXIBLE LINE	11 - PITOT TUBE & INCLINED MANOMETER
6 - VACUUM GAGE	12 - POTENTIOMETER

FIGURE 3-1: MODIFIED EPA PARTICULATE SAMPLING TRAIN
AUGUST 18,1977, FEDERAL REGISTER

nozzle, probe, flexible teflon line, first two impingers, and their connecting glassware were rinsed with deionized, distilled water. The samples were put in glass containers with teflon-lined caps as follows:

Container #1 - nozzle, probe and teflon line washes.

Container #2 - contents of the first impinger and the distilled water wash of the impinger and its glassware connector.

Container #3 - contents of the second impinger and the distilled water wash of the impinger and its glassware connector.

Container #4 - contents of the third, fourth and fifth impingers and the 1N H_2SO_4 wash of these impingers and their connecting glassware.

These samples containers were then returned to TRC for urea and ammonia analysis.

3.5.3 Sample Analysis

At TRC the volumes of each sample were measured and the samples were analyzed for ammonia with the specific ion electrode method and for urea with the p-dimethylaminobenzaldehyde (PDAB) method with preliminary distillation. Analyses were performed within 20 days of sample collection. For the urea analysis, a sodium borate buffer and NaOH were added to each sample to adjust the pH to 9.5 or greater. The samples were then boiled to remove ammonia, and the PDAB color reagent was added to the residue. The solution absorbance was then measured in a spectrophotometer.

An additional 1 ml concentrated hydrochloric acid per liter of solution was added to acid impinger sample solutions prior to the absorbance readings. This was done in order to remove the turbidity that resulted upon addition of the PDAB color reagent. Urea standards were prepared with the same acid content as the samples. Sample absorbances were converted to urea concentration with the calibration curve drawn from the analysis of these standards. No problems were encountered in the analysis of these samples.

APPENDIX A

UREA SAMPLING AND ANALYSIS PROCEDURES

Includes:

A.1 Original Procedure - August 1978*
A.2 Modified Procedure - August 1979*
A.3 Modified Procedure - January 1980*
A.4 Proposed Reference Method 28*
A.5 Kjeldahl Analysis Procedure

* p-dimethylaminobenzaldehyde analysis method

APPENDIX A.1

ORIGINAL PROCEDURE - AUGUST 1978

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DETERMINATION OF PARTICULATE, UREA, AND AMMONIA EMISSIONS FROM UREA PLANTS

1. Principle and Applicability

1.1 Principle. A gas sample is extracted isokinetically from the stack. The urea and the ammonia are separated and both are measured by colorimetric procedures.

1.2 Applicability. This method is applicable for the determination of urea manufacturing facilities.

Interferences for the urea determination are hydroxylamine in a mole ratio of 8:1 and ammonium ion in a ratio of 15:1. Hydrazine and semicarbazide interfere at a 1:1 mole ratio.

Possible interferences with the ammonia procedure are calcium, magnesium, iron and sulfide.

2. Apparatus

2.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 1. Complete construction details are given in APTD-0581 (Citation 2 in Section 7); commercial models of this train are also available. For changes from APTD-0581 and for allowable modifications of the train shown in Figure 1, see the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD-0576 (Citation 3 in Section 7). Since correct usage is important in obtaining valid results, all users should read APTD-0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. The sampling train consists of the following components:

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2.1.1 Probe Nozzle. Stainless steel (316) or glass with sharp, leading edge. The angle of tapes shall be $\leq$ 30° and the tapes shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. If made of stainless steel, the nozzle shall be constructed from seamless tubing; other materials of construction may be used subject to the approval of the Administrator.

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g. 0.32 to 1.27 cm (1/8 to 1/2 in.) - or larger if higher volume sampling trains are used inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in Section 5.

2.1.2 Probe Liner. Borosilicate or quartz glass tubing with a heating system capable of maintaining a gas temperature at the exit end during sampling of 120 $\pm$ 14°C (248 $\pm$ 25°F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. (The tester may opt to operate the equipment at a temperature lower than that specified.) Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-0581 and utilizing the calibration curves of APTD-0576 (or calibrated according to the procedure outlined in APTD-0576) will be considered acceptable.

Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480°C (900°F); quartz liners shall be used for temperatures between 480 and 900°C (900 and 1650°F). Both

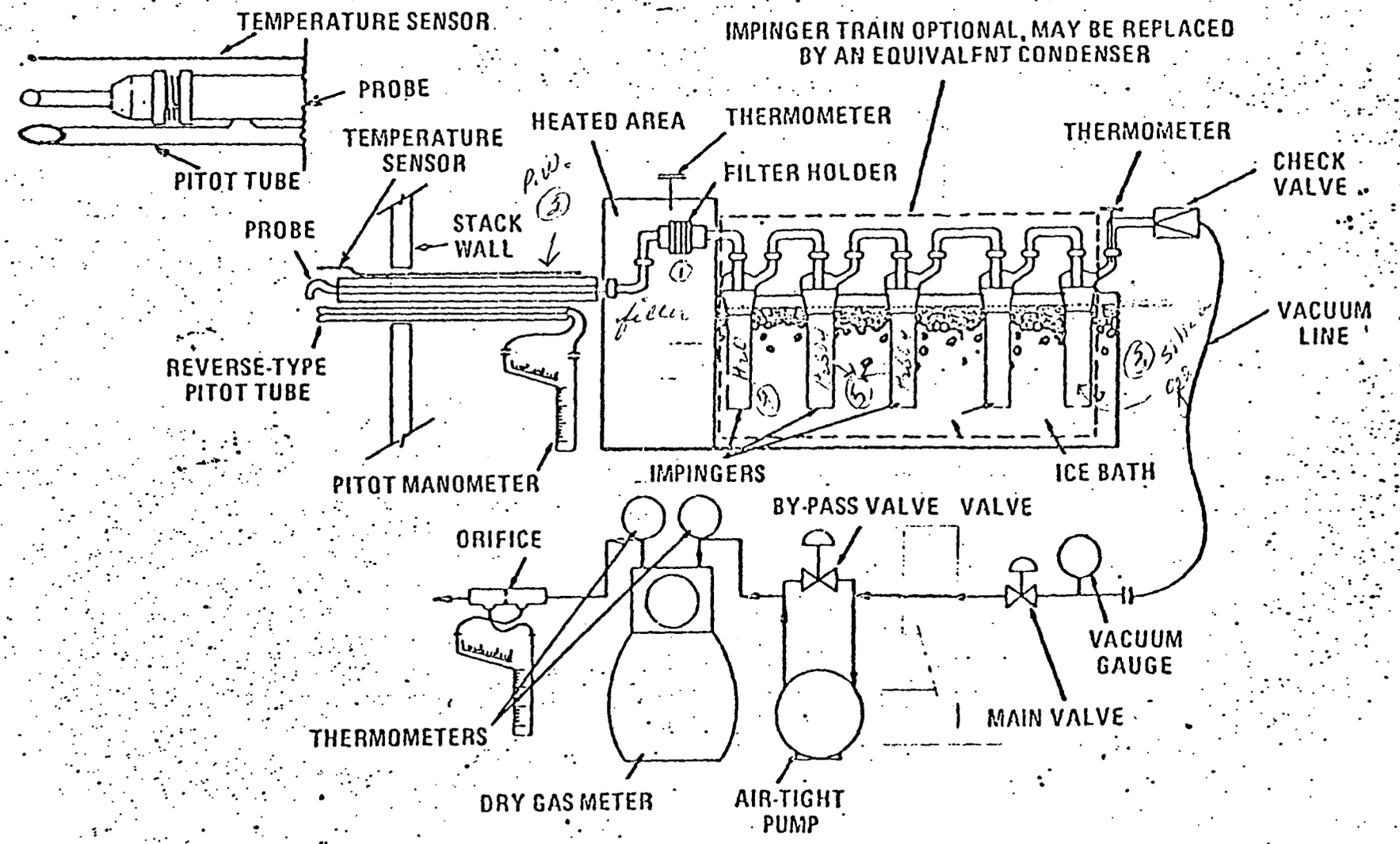

Figure 5-1. Particulate-sampling train.

types of liners may be used at higher temperatures than specified for short periods of time, subject to the approval of the Administrator. The softening temperature for borosilicate is 820°C (1508°F), and for quartz it is 1500°C (2732°F).

Whenever practical, every effort should be made to use borosilicate or quartz glass probe liners. Alternatively, metal liners (e.g., 316 stainless steel, Incoloy 825,[1] or other corrosion resistant metals) made of seamless tubing may be used, subject to the approval of the Administrator.

2.1.3 Pitot Tube. Type S, as described in Section 2.1 of Method 2, or other device approved by the Administrator. The pitot tube shall be attached to the probe (as shown in Figure 5-1) to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of Method 2.

2.1.4 Differential Pressure Gauge. Inclined manometer or equivalent device (two), as described in Section 2.2 of Method 2. One manometer shall be used for velocity head (Δp) readings, and the other, for orifice differential pressure readings.

2.1.5 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other materials of construction (e.g., stainless steel, Teflon, Viton) may be used, subject to the approval of the Administrator. The holder design shall provide a positive

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[1]Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).

2.1.6 Filter Heating System. Any heating system capable of maintaining a temperature around the filter holder during sampling of 120 ± 14°C (248 ± 25°F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. Alternatively, the tester may opt to operate the equipment at a temperature lower than that specified. A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than the one shown in APTD-0581 may be used.

2.1.7 Impingers--Five as Shown in Figure 1. The first and third shall be of the Greenburg-Smith design with standard tips. The second, fourth, and fifth shall be of the Greenburg-Smith design, modified by replacing the insert with an approximately 13 millimeter (0.5 in) I.D. glass tube, having an unconstricted tip located 13 mm (0.5 in.) from the bottom of the flask. Similar collection systems, which have been approved by the Administrator, may be used.

2.1.8 Metering System. Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 5-1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of

the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD-0581 or APTD-0576 may be used provided that the specifications of this method are met.

2.1.9 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.10 Gas Density Determination Equipment. Temperature sensor and pressure gauge, as described in Sections 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration, such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see Method 2, Figure 2-7). As a second alternative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube. (This alternative is

subject to the approval of the Administrator.)

2.2 Sample Recovery. The following items are needed:

2.2.1 Probe-Liner and Probe-Nozzle Brushes. Nylon bristle brushes with stainless steel wire handles. The probe brush shall have extensions (at least as long as the probe) of stainless steel, Nylon, Teflon, or similarly inert material. The brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

2.2.2 Wash Bottles--Two. Glass wash bottles are recommended; polyethylene wash bottles may be used at the option of the tester. It is recommended that acetone not be stored in polyethylene bottles for longer than a month.

2.2.3 Glass Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak_free and resistant to chemical attack by acetone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Alternatively, polyethylene bottles may be used.

2.2.4 Petri Dishes. For filter samples, glass or polyethylene, unless otherwise specified by the Administrator.

2.2.5 Graduated Cylinder and/or Balance. To measure condensed water to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. Any of these balances is suitable for use here and in Section 2.3.4.

2.2.6 Plastic Storage Containers. Air_tight containers to store silica gel.

2.2.7 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

2.2.8 Funnel. Glass or polyethylene, to aid in sample recovery.

2.3 Analysis.

2.3.1 Pipettes. Volumetric type 0.5-ml, 1-ml, 2-ml, 5-ml, 8-ml, 10-ml, 20-ml, and 25-ml sizes.

2.3.2 Volumetric Flasks. 25-ml size, 100-ml size, 250-ml size, 500-ml size and 1000-ml size.

2.3.3 Graduated Cylinder. 100-ml size.

2.3.4 Spectrophotometer. To measure absorbance at 405 manometers and 420 manometers.

2.3.5 Sample Cells. Two matched absorbance cells to fit the spectrophotometer.

3. Reagents

Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

3.1 Sampling.

3.1.1 Water. Deionized, distilled to conform to ASTM specification D 1193-74, type 3. At the option of the Analyst, the $KMNO_4$ test for oxidizable organic matter may be omitted when high concentration of organic matter are not expected to be present.

3.1.2 Sulfuric Acid, 1.0.N. Dilute 28 ml of concentrated, ACS grade sulfuric acid to 1 liter with deionized, distilled water.

3.2 Sample Recovery.

3.2.1 Water. Deionized, distilled, as in 3.1.1.

3.2.2 Sulfuric Acid, 1.0 N. As in 3.1.2.

3.2.3 Acetone--Reagent Grade, $\leq$ 0.001 percent residue, in glass bottles, is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values ($\leq$ 0.001 percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

3.3 Analysis.

3.3.1 Water. Deionized, distilled, as in 3.1.1.

3.3.2 Annhydrous Mercuric Iodide ($Hg\ I_2$). ACS grade.

3.3.3 Potassium Iodide (KI). ACS grade.

3.3.4 Sodium Hydroxide (NaOH). ACS grade.

3.3.5 Stock standard Ammonium Chloride Solution. Dissolve 3.141 g of ammonium chloride (NH_4Cl) in 1.0N H_2SO_4 in a 1-liter volumetric flask and dilute to exactly 1 liter with 1.0N H_2SO_4. One milliliter of this solution contains 1.0 mg of ammonia (NH_3).

3.3.6 Working Standard Ammonium Chloride Solution. Dilute 10 ml of the stock standard solution to 1 liter with 1.0 N H_2SO_4 in a 1-liter volumetric flask. One milliliter of this solution contains 10 μg of ammonia (NH_3).

3.3.7 Sodium Hydroxide, 10 N. Dissolve 40 grams of NaOH in a 100-ml volumetric flask and dilute exactly to 100-ml with deionized distilled water.

3.3.8 Nessler Reagent. Dissolve 160 g of NaOH in 50 of deionized distilled water in a 1-liter volumetric flask. Allow to cool. Dissolve 100 g of mercuric iodide and 70 g of potassium iodide in a small volume of deionized distilled water and while stirring add to the sodium hydroxide solution. Dilute to exactly 1 liter with deionized, distilled water. This reagent is stable up to 1 year.

3.3.9 Ethyl Alcohol, 95 Percent. ACS grade.

3.3.10 P-dimethylaminobenzaldehyde. ACS grade.

3.3.11 Hydrochloric, Concentrated (36.5 - 38 percent by weight). ACS grade.

3.3.12 Stock Standard Urea Solution. Dissolve 5.00 g of urea in 500 ml of distilled, deionized water in a 1-liter flask and dilute to exactly 1 liter with deionized, distilled water.

3.3.13 Working Standard Urea Solution. Pipette 25 ml of stock standard urea solution into a 100-ml volumetric flask and dilute to exactly 100 ml with deionized distilled water. One milliliter of this solution contains 1.250 mg of urea.

3.3.14 Urea Color Reagent. Prepare the color reagent by dissolving 2.000 g of P-dimethylaminobenzaldehyde in a mixture of 100 ml of 95 percent ethyl alcohol and 10 ml of hydrochloric acid.

4. Procedure

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation. All the components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified herein.

Weigh several 200 to 300 g portions of silica gel in ai containers to the nearest 0.5 g. Record the total weight of the silica gel plus container, one each container. As an alternative, the silica gel need not be preweighed, but may be weighed directly in its impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Label filters of the proper diameter on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or plastic petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

Desiccate the filters at 20 ± 5.6°C (68 ± 10°F) and ambient pressure for at least 24 hours and weigh at intervals of at least 6 hours to a constant weight, i.e., ≤0.5 mg change from previous weighing; record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent. Alternatively (unless otherwise specified by the Administrator), the filters may be oven dried at 105°C (220°F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Administrator.

4.1.2 Preliminary Determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is

recommended that a leak-check of the pitot lines (see Method 2, Section 3.1) be performed. Determine the moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, Section 3.6; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particulate sample run.

Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of Method 2).

Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 min. (or some greater time interval as specified by the Administrator), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

The sampling time at each point shall be the same. It is recommended that the number of minutes sampled at each point be an integer or an integer plus onehalf minute, in order to avoid timekeeping errors.

In some circumstances, e.g., batch cycles, it may be neccesary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

4.1.3 Preparation of Collection Train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Place 75 ml of water in the first impinger, 100 ml of 1.0 N sulfuric acid into each of the next two impingers, leave the fourth impinger empty and transfer 200 - 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

When glass liners are used, install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260°C (500°F) and an asbestos string gasket when temperatures are higher. See APTD-0576 for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. When metal liners are used, install the nozzle as above or by a leak-free direct mechanical connection. Mark

proper distance into the stack or duct for each sampling po

Set up the train as in Figure 1, using (if necessary) a very light coat of silicone grease on all ground glass joints, greasing only the outer portion (see APTD-0576) to avoid possibility of contamination by the silicone grease. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack gas.

Place crushed ice around the impingers.

4.1.4 Leak-Check Procedures.

4.1.4.1 Pretest Leak-Check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, the following procedure shall be used.

After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum.

Note: A lower vacuum may be used, provided that it is not exceeded during the test.

If an asbestos string is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first plugging the inlet to the filter holder (cyclone, if applicable) and pulling a 380 mm Hg (15 in. Hg) vacuum (see Note immediately above). Then connect the probe to the train and leak-check at about 25 mm Hg (1 in. Hg) vacuum; alternatively, the probe may be leak-checked with

the rest of the sampling train, in one step, at 380 mm Hg (15 in. Hg) vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.02 cfm), whichever is less, are unacceptable.

The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until the desired vacuum is reached. Do not reverse direction of bypass valve; this will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak check as shown below and start over.

When the leak-check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable) and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder and silica gel from being entrained backward into the third impinger.

4.1.4.2 Leak-Checks During Sample Run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary, a leak-check shall be conducted immediately before the change is made. The leak-check shall be done according to the procedure outlined in Section 4.1.4.1 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate

(whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and plan to correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

Immediately after component changes, leak-checks are optional; if such leak-checks are done, the procedure outlined in Section 4.1.4.1 above shall be used.

4.1.4.3 Post-test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done in accordance with the procedures outlined in Section 4.1.4.1, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

4.1.5 Particulate Train Operation. During the sampling run, maintain an isokinetic sampling rate (within 10 percent of true isokinetic unless otherwise specified by the Administrator) and a temperature around the filter of 120 ± 14°C (248 ± 25°F), or such other

temperature as specified by an applicable subpart of the standards or approved by the Administrator.

For each run, record the data required on a data sheet such as the one shown in Figure 5-2. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted. Take other readings required by Figure 5-2 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

Clean the portholes prior to the test run to minimize the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are up to temperature, and that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient is 0.85 $\pm$ 0.02, and the stack gas equivalent density (dry molecular weight) is equal to 29 $\pm$ 4. APTD-0576 details the procedure for using the nomographs. If C_p and M_d are outside the above stated ranges, do not use the nomographs unless appropriate steps (See citation 7 in Section 7) are taken to compensate for the deviations.

PLANT _____

LOCATION _____

OPERATOR _____

DATE _____

RUN NO. _____

SAMPLE BOX NO. _____

METER BOX NO. _____

METER $\Delta H_@$ _____

C FACTOR _____

PITOT TUBE COEFFICIENT, C_p _____

SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE _____

BAROMETRIC PRESSURE _____

ASSUMED MOISTURE, % _____

PROBE LENGTH, m (ft) _____

NOZZLE IDENTIFICATION NO. _____

AVERAGE CALIBRATED NOZZLE DIAMETER, cm (in.) _____

PROBE HEATER SETTING _____

LEAK RATE, m^3/min. (cfm) _____

PROBE LINER MATERIAL _____

STATIC PRESSURE, mm Hg (in. Hg) _____

FILTER NO. _____

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	VACUUM mm Hg (in Hg)	STACK TEMPERATURE (T_S) °C (°F)	VELOCITY HEAD (ΔP_S), mm (in.) H_2O	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER mm H_2O (in. H_2O)	GAS SAMPLE VOLUME m^3 (ft^3)	GAS SAMPLE TEMPERATURE AT DRY GAS METER		FILTER HOLDER TEMPERATURE, °C (°F)	TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °C (°F)
							INLET °C (°F)	OUTLET °C (°F)		
TOTAL							Avg.	Avg.		
AVERAGE							Avg.			

Figure 5-2. Particulate field data.

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to prevent water from backing into the filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

Traverse the stack cross-section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes; this minimizes the chance of extracting deposited material.

During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper level; add more ice and, if necessary, salt to maintain a temperature of less than 20°C (68°F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of a sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak-check (see Section 4.1.4.2). The total particulate weight shall include the summation of all filter assembly catches.

A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or, in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

Note that when two or more trains are used, separate analyses of the front-half and (if applicable) impinger catches from each train shall be performed, unless identical nozzle sizes were used on all trains, in which case, the front-half catches from the individual trains may be combined (as may the impinger catches) and one analysis of front-half catch and one analysis of impinger catch may be performed. Consult with the Administrator for details concerning the calculation of results when two or more trains are used.

At the end of the sample run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check, as outlined in Section 4.1.4.3. Also, leak-check the pitot lines as described in Method 2, Section 3.1; the lines must pass this leak-check, in order to validate the velocity head data.

4.1.6 Calculation of Percent Isokinetic. Calculate percent isokinetic (see Calculations, Section 6) to determine whether the run was valid or another test run should be made. If there was difficulty in maintaining isokinetic rates due to source conditions, consult with the Administrator for possible variance on the isokinetic rates.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, thus drawing water from the impingers into the filter holder.

Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the filter inlet where the probe was fastened and cap it. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger or condenser and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the impingers or condenser. After wiping off the silicone grease, cap off the filter holder outlet and impinger inlet. Either ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

Save a portion of the acetone used for cleanup as a blank. Take 200 ml of this acetone directly from the wash bottle being used and place it in a glass sample container labeled "acetone blank."

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

Container No. 1. Carefully remove the filter from the filter holder and place it in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the petri dish any particulate matter and/or filter fibers which adhere to the filter holder gasket, by using a dry Nylon bristle brush and/or a sharp-edged blade. Seal the container.

Container No. 2. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis. Perform the acetone rinses as follows:

Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a Nylon bristle brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse the inside parts of the Swagelok fitting with acetone in a similar way until no visible particles remain.

Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Let the acetone drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Follow the acetone rinse with a probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

It is recommended that two people be used to clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

After ensuring that all joints have been wiped clean of silicone grease, clean the inside of the front half of the filter holder by rubbing the surfaces with a Nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone, also (if applicable). After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container to clearly identify its contents.

Container No. 3. Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water

Plant _____

Date _____

Run No. _____

Filter No. _____

Amount liquid lost during transport _____

Acetone blank volume, ml _____

Acetone wash volume, ml _____

Acetone blank concentration, mg/mg (equation 5-4) _____

Acetone wash blank, mg (equation 5-5) _____

CONTAINER NUMBER	WEIGHT OF PARTICULATE COLLECTED, mg		
	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN
1			
2			
TOTAL			
	Less acetone blank		
	Weight of particulate matter		

	VOLUME OF LIQUID WATER COLLECTED		
	IMPINGER VOLUME, ml.	SILICA GEL WEIGHT, g	
FINAL			
INITIAL			
LIQUID COLLECTED			
TOTAL VOLUME COLLECTED		g*	ml

*CONVERT WEIGHT OF WATER TO VOLUME BY DIVIDING TOTAL WEIGHT INCREASE BY DENSITY OF WATER (1g/ml).

$$\frac{\text{INCREASE, g}}{\text{1 g/ml}} = \text{VOLUME WATER, ml}$$

Figure 5-3. Analytical data.

or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for container No. 3 in Section 4.3.

Container No. 4. Measure and record the volume of the first impinger. Then transfer the contents to a storage container. Rinse the first impinger and the connecting glassware with water and add the rinse water to the container. Mark the level of the liquid on the container and identify the sample container.

Container No. 5 Measure and record the volume of the second and third impingers. Then transfer the contents to a storage container. Rinse the impinger and connecting glassware with 1.0 N sulfuric acid and add the rinsings to the sample container. Mark the level of liquid on the container and identify the sample container.

4.3 Analysis. Record the data required on a sheet such as the one shown in Figure 5-3. Handle each sample container as follows:

4.3.1 Container No 1. Leave the contents in the shipping container or transfer the filter and any loose particulate from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg. For purposes of this section, 4.3, the term "constant weight" means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings.

Place the filter in a beaker with 50 ml of deionized, distilled water and place the beaker in an ultrasonic bath for 15 minutes. Combine this solution with the solution from Container No. 4 as discussed under Section 4.3.4.

4.3.2 Container No. 2. Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ± 1 ml or gravimetrically to ± 0.5 g. Transfer the contents to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Add 50 ml of deionized distilled water to the residue in the beaker and place the beaker in an ultrasonic bath for 15 minutes. Combine this solution with the solution from Container No. 4 as discussed under Section 4.3.4.

4.3.3 Container No. 3. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

4.3.4 Container No. 4. Quantitatively transfer the contents of Container No.4 to a 250-ml volumetric flaks. Add to this flask the extracts from Containers 1 and 2. Dilute to exactly 250 ml with deionized, distilled water. Pipette 10 ml of this solution into a 25-ml volumetric flask and add 10 ml of the urea color reagent. Dilute to exactly ~~10~~ 25 ml with deionized, distilled water. Mix well and allow to stand for at least 10 minutes for full color development. Measure the absorbance of the solution at 420 ~~NM~~ nm using the blank solution (Section 5.5) as a zero reference. Dilute the sample and the blank with equal amounts of deionized distilled water if the absorbance exceeds that of the 5.00 mg urea standard.

4.3.5 Container No. 5. Quantitatively transfer the contents of Container No. 5 to a 1-liter volumetric flask. Rinse the container and cap with several portions of 1.0 N sulfuric acid and transfer to the flask. Dilute to exactly 1 liter with 1.0N sulfuric acid. Pipette 10 ml of the sample from the 1-liter flask into a 500 ml-volumetric flask and dilute to exactly 500 ml with 1.0 N H_2SO_4. Pipette 20 ml of this solution into a 25-ml volumetric flask. Add 10 N sodium hydroxide dropwise to the flask until the pH is between eight and ten. Then add 0.5 ml of Nessler reagent and dilute to exactly 25 ml with deionized distilled water. Mix well and allow to stand for the same amount of time as the standards used for calibration. Measure the absorbance at 405 nm using the blank solution (Paragraph 5.5) as a zero reference. Dilute the sample and the blank with equal amounts of deionized distilled water if the absorbance exceeds that of the 100 μg NH_3 solution.

4.3.6 "Acetone Blank" Container. Measure acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

5. Calibration

Maintain a laboratory log of all calibrations.

5.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and

low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

5.2 Pitot Tube. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of Method 2.

5.3 Metering System. Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry gas meter dial readings to correspond to the wet test meter readings, calibration factors may be used to mathematically correct the gas meter dial readings to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases, the following leak-check procedure is

pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is

suggested: make a 10-minute calibration run at 0.00057 m^3/min (0.02 cfm); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by 10, to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 cfm).

After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate orifice setting (based on the previous field test), with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and

the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

Alternative procedures, e.g., using the orifice meter coefficients, may be used, subject to the approval of the Administrator.

Note: If the dry gas meter coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

5.4 Probe Heater Calibration. The probe heating system shall be calibrated before its initial use in the field according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

5.5 Temperature Gauges. Use the procedure in Section 4.3 of Method 2 to calibrate in-stack temperature gauges. Dial thermometers, such as are used for the dry gas meter and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

5.6 Leak Check of Metering System Shown in Figure 5-1. That portion of the sampling train from the pump to the orifice meter should be leak checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 5-4): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber

tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

5.7 Barometer. Calibrate against a mercury barometer.

5.8 Determination of Spectrophotometer Calibration Factor K.

5.8.1 Urea Analysis. Add 0.0, 1.0, 2.0, 3.0, and 4.0 ml of working standard urea solution to a series of five 25-ml volumetric flasks. Pipette 10 ml of the urea color reagent into the flask and dilute to exactly 25 ml with deionized distilled water. Mix well and allow each to stand for at least 10 minutes for color development. Measure the absorbance of each standard at 420 nm. The calibration procedure must be repeated each day that samples are analyzed. Calculate the spectrophotometer calibration factor as follows:

$$K_{cu} = 1250 \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2 + A_5^2}$$

Where:

K_{cu} = Calibration factor for urea analysis.

A_1 = Absorbance of the 1250 µg standard

A_2 = Absorbance of the 2500 µg standard.

A_3 = Absorbance of the 3750 µg standard.

A_4 = Absorbance of the 5000 µg standard.

5.8.2 Ammonia Analysis: Add 0.0, 1.0, 2.0, 5.0, 8.0, and 10.0 ml of working standard ammonium chloride solution to a series of six 25-ml volumetric flasks. Adjust the total volume of solution in each

6.5 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \quad \text{, Equation 5-3}$$

Note: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 5-3), and a second from the assumption of saturated conditions. The lower of the two values of B_{ws} shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the Note of Section 1.2 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 5-2 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is $\pm$ 1°C (2°F).

6.6 Acetone Blank Concentration.

$$C_a = \frac{m_a}{V_a \rho_a}$$

6.7 Acetone Wash Blank.

$$W_a = C_a V_{aw} \rho_a$$

6.8 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from containers 1 and 2 less the acetone blank (see Figure 5-3). Note: Refer to Section 4.1.5 to assist in calculation of results involving two or more filter assemblies or two or more sampling trains.

6.9 Particulate Concentration.

$$C_s = (0.001\ g/mg)\ (M_a/V_{m(std)})$$ Equation 6

6.10 Total Mass of Urea Per Sample.

$$M_u = K_{cu}\ AF\ \frac{V_{al}}{V_{Soln}}$$ Equation 7

6.11 Urea Concentration.

$$C_u = K_2\ \frac{M_u}{V_{sc}}$$ Equation 8

Where:

$K_2 = 10^3\ \frac{Mg/m^3}{\mu g/ml}$ for metric units.

$6.243 \times 10^{-5}\ \frac{lb/SCF}{\mu g/ml}$ for English units.

6.12 Total Mass of NH_3 Per Sample.

$$M_{NH_3} = K_{C\ NH_3}\ AF\ \frac{V_{al}}{V_{soln}}$$ Equation 9

6.13 Ammonia Concentration.

$$C_{NH_3} = K_2\ \frac{M}{V_{sc}}$$ Equation 10

Where: $K_2 = 10^3\ \frac{mg/m^3}{\mu g/ml}$ for Metric units.

$= 6.243 \times 10^{-5}\ \frac{lb/SCF}{\mu g/ml}$ for English units.

APPENDIX A.2

MODIFIED PROCEDURE - AUGUST 1979

8/19/79

~~2/22/79~~

DETERMINATION OF PARTICULATE, UREA, AND AMMONIA EMISSIONS FROM UREA PLANTS

1. Principle and Applicability

1.1 Principle. A gas sample is extracted isokinetically from the stack. The urea and the ammonia are separated by distillation, the urea is converted to ammonia, and both are measured by a colorimetric procedure.

1.2 Applicability. This method is applicable for the determination of urea and ammonia from urea manufacturing facilities.

Possible interferences with the ammonia procedure are calcium, magnesium, iron and sulfide.

2. Apparatus

2.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 1. Complete construction details are given in APTD-0581 (Citation 2 in Section 7); commercial models of this train are also available. For changes from APTD-0581 and for allowable modifications of the train shown in Figure 1, see the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD-0576 (Citation 3 in Section 7). Since correct usage is important in obtaining valid results, all users should read APTD-0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. The sampling train consists of the following components:

2.1.1 Probe Nozzle. Stainless steel (316) or glass with sharp, leading edge. The angle of taper shall be $\leq 30^{0}$ and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. If made of stainless steel, the nozzle shall be constructed from seamless tubing; other materials of construction may be used subject

to the approval of the Administrator.

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g. 0.32 to 1.27 cm (1/8 to 1/2 in.) - or larger if higher volume sampling trains are used - inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in Section 5.

2.1.2 Probe Liner. Borosilicate or quartz glass tubing with a heating system capable of maintaining a gas temperature at the exit end during sampling of no greater than 80°C (176°F) 120 ± 14°C (248 ± 25°F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. (The tester may opt to operate the equipment at a temperature lower than that specified).

Whenever practical, every effort should be made to use borosilicate or quartz glass probe liners. Alternatively, metal liners (e.g., 316 stainless steel, Incoloy 825,[1] or other corrosion resistant metals) made of seamless tubing may be used, subject to the approval of the Administrator.

2.1.3 Pitot Tube. Type S, as described in Section 2.1 of Method 2, or other device approved by the Administrator. The pitot tube shall be attached to the probe (as shown in Figure 5-1) to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of Method 2.

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[1] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

2.1.4 Differential Pressure Gauge. Inclined manometer or equivalent device (two), as described in Section 2.2 of Method 2. One manometer shall be used for velocity head (Δp) readings, and the other, for orifice differential pressure readings.

2.1.5 Impingers--Six as shown in Figure 1. The first and third shall be of the Greenburg-Smith design with standard tips. The second, fourth, and fifth shall be of the Greenburg-Smith design, modified by replacing the insert with an approximately 13 millimeter (0.5 in) I.D. glass tube, having an unconstricted tip located 13 mm (0.5 in) from the bottom of the flask. Similar collectiln systems, which have been approved by the Administrator, may be used.

2.1.6 Metering System. Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 5-1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD-0581 or APTD-0576 may be used provided that the specifications of this method are met.

2.1.9 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation

differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.10 Gas Density Determination Equipment. Temperature sensor and pressure gauge, as described in Sections 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration, such that the tip of the senor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see Method 2, Figure 2-7). As a second alternative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube. (This alternative is subject to the approval of the Administratior).

2.2 Sample Recovery. The following items are needed:

2.2.1 Probe-Liner and Probe-Nozzle Brushes. Nylon bristle brushes with stainless steel wire handles. The probe brush shall have extensions (at least as long as the probe) of stainless steel, Nylon, Teflon, or similarly inert material. The brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

2.2.2 Wash Bottles--Two. Glass wash bottles are recommended; polyethylene wash bottles may be used at the option of the tester.

2.2.3 Glass Sample Storage Containers. Chemically resistant,

borosilicate glass bottles 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free. (Narrow mouth glass bottles have been found to be less prone to leakage). Alternatively, polyethylene bottles may be used.

2.2.4 Petri Dishes. For filter samples, glass or polyethylene, unless otherwise specified by the Administrator.

2.2.5 Graduated Cylinder and/or Balance. To measure condensed water to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. Any of these balances is suitable for use here and in Section 2.3.4.

2.2.6 Plastic Storage Containers. Air-tight containers to store silica gel.

2.2.7 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

2.2.8 Funnel, Glass or po-yethylene, to aid in sample recovery.

2.3 Analysis.

2.3.1 Pipettes. Volumetric type 0.5-ml, 2-ml, 5-ml, 8-ml, 10-ml, 20-ml, and 25-ml sizes.

2.3.2 Volumetric Flasks. 25-ml size, 100-ml size, 250-ml size, 500-ml size and 1000-ml size.

2.3.3 Graduated Cylinder. 100-ml size.

2.3.4 Distillation Apparatus.

2.3.4.1 Kjeldahl Flasks. At least two 800 ml size.

2.3.4.2 Connecting bulb. To connect the kjeldahl flask to the condenser and prevent liquid carry over.

W s

2.3.4.3 Condenser. Glass-wert type or equivalent.

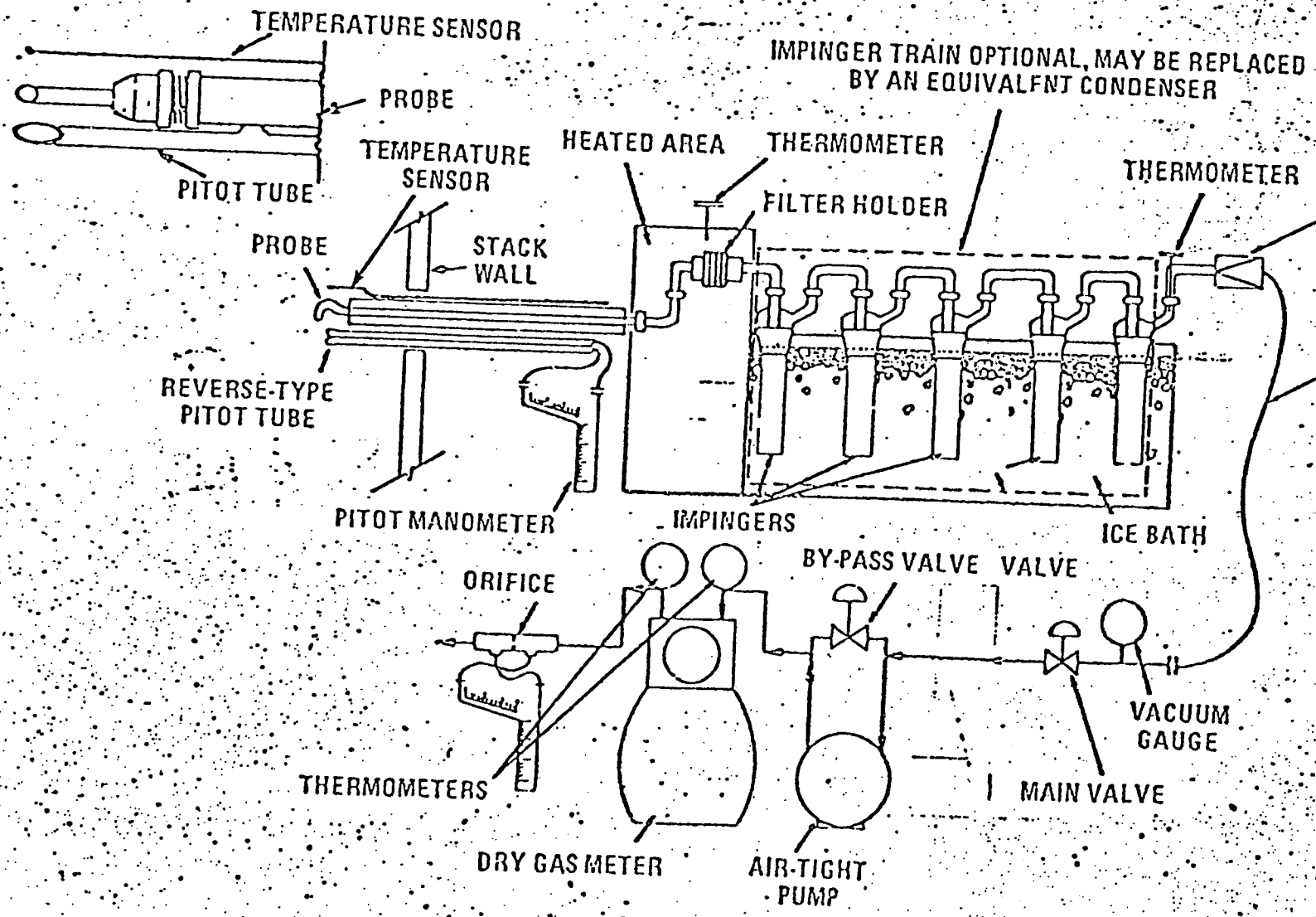

Figure 5-1. Particulate-sampling train.

2.3.4.4 Receiving Adapter. To connect the condenser to the receiving flask.

2.3.5 Erlenmeyer Flasks. 500 ml size.

2.3.6 Spectrophotometer. To measure absorbance at 405 nanometers.

2.3.7 Sample Cells. Two matched absorbance cells to fit the spectrophotometer.

3. Reagents

Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

3.1 Sampling.

3.1.1 Water. Deionized, distilled to conform to ASTM specification D 1193-74, type 3. At the option of the Analyst, the $KMNO_4$ test for oxidizable organic matter may be omitted when high concentration of organic matter are not expected to be present.

3.1.2 Sulfuric Acid, 1.0.N. Dilute 28 ml of concentrated, ACS grade sulfuric acid to 1 liter with deionized, distilled water.

3.2 Sample Recovery.

3.2.1 Water. Deionized, distilled, as in 3.1.1.

3.2.2 Sulfuric Acid, 1.0 N. As in 3.1.2.

3.3 Analysis.

3.3.1 Water. Deionized, distilled, as in 3.1.1.

3.3.2 Annhydrous Mercuric Iodide ($Hg\ I_2$). ACS grade.

3.3.3 Potassium Iodide (KI). ACS grade.

3.3.4 Sodium Hydroxide (NaOH). ACS grade.

3.3.5 Stock standard Ammonium Chloride Solution. Dissolve 3.141 g of

ammonium chloride (NH_4Cl) in deionized distilled water in a 1-liter volumetric flask and dilute to exactly 1 liter with deionized distilled water. One milliliter of this solution contains 1.0 mg of ammonia (NH_3).

3.3.6 Working Standard Ammonium Chloride Solution. Dilute 10 ml of the stock standard solution to 1 liter with deionized distilled water in a 1-liter volumetric flask. One milliliter of this solution contains 10 µg of ammonia (NH_3).

3.3.7 Sodium Hydroxide, 10 N. Dissolve 40 grams of NaOH in a 100-ml volumetric flask and dilute exactly to 100-ml with deionized distilled water.

3.3.8 Nessler Reagent. Dissolve 160 g of NaOH in 500 ml of deionized distilled water in a 1-liter volumetric flask. Allow to cool. Dissolve 100 g of mercuric iodide and 70 g of potassium iodide in a small volume of deionized distilled water and while stirring add to the sodium hydroxide solution. Dilute to exactly 1 liter with deionized, distilled water. This reagent is stable up to 1 year.

3.3.9 Borate Buffer. Dissolve 2.5 g of sodium tetraborate, $Na_2B_4O_7$, or 4.8 gof the decahydrate $Na_2B_4O_7 \cdot 10\ H_2O$, in 500 ml of distilled deionized water in a 1 liter volumetric flask. Add 88 ml of 0.1 N NaOH solution and dilute to exactly 1 liter with distilled deionized water.

3.3.10 Sodium Hydroxide 6 N. Dissolve 240 g of NaOH in 800 ml of distilled deionized water in a 1 liter flask. Dilute to exactly 1 liter with distilled deionized water.

3.3.11 Sodium Thiosulfute Dechlorinating Agent. Dissolve 3.5 g of $Na_2S_2O_3 \cdot 5H_2O$ in 800 ml of water in a 1 liter volumetric flask and dilute to exactly 1 liter with distilled deionized water.

3.3.12 Sodium Hydroxide 1 N. Dissolve 40 g of NaOH in 800 ml of

distilled deionized water in a 1 liter flask and dilute to exactly 1 liter with distilled deionize water.

3.3.13 Sulfuric Acid 1 N. Slowly add 56 ml of concentrated sulfuric to 800 ml of distilled deionized water in a 1 liter flask and dilute to exactly 1 liter with distilled deionized water.

3.3.14 Ethyl Alcohol, 95 Percent. ACS grade.

3.3.15 P-dimethylaminobenzaldehyde. ACS grade.

3.3.16 Hydrochloric, Concentrated (36.5 - 38 percent by weight). ACS grade.

3.3.17 Stock Standard Urea Solution. Dissolve 5.00 g of urea in 500 ml of distilled, deionized water in a 1-liter flask and dilute to exactly 1 liter with deionized, distilled water.

3.3.18 Working Standard Urea Solution. Pipette 25 ml of stock standard urea solution into a 100-ml volumetric flask and dilute to exactly 100 ml with deionized distilled water. One milliliter of this solution contains 1.250 mg of urea.

3.3.19 Urea Color Reagent. Prepare the color reagent by dissolving 2.000 g of P-dimethylaminobenzaldehyde in a mixture of 100 ml of 95 percent ethyl alcohol and 10 ml of hydrochloric acid.

4. Procedure

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation. All the components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified herein.

otherwise specified herein.

Weigh several 200 to 300 g portions of silica gel in air-tight containers to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel need not be preweighed, but may be weighed directly in its impinger or sampling holder just prior to train assembly.

4.1.2 Preliminary Determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it recommended that a leak-check of the pitot lines (see Method 2, Section 3.1) be performed. Determine the moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, Section 3.6; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particulate sample run.

Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of Method 2).

Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific

industry such that (1) the sampling time per point is not less than 2 min. (or some greater time interval as specified by the Administrator), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

The sampling time at each point shall be the same. It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors.

In some circumstances, e.g., batch cycles, it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

4.1.3 Preparation of Collection Train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Place 75 ml of water in the first two impingers, 100 ml of 1.0 N sulfuric acid into each of the next two impingers, leave the fifth impinger empty and transfer 200 - 300 g of preweighed silica gel from its container to the sixth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later used in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

When glass liners are used, install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260°C (500°F) and an asbestos string gasket when temperatures are higher. See APTD-0576 for details. Other connecting systems using either 316 stainless steel or Teflon ferrules

may be used. When metal liners are used, install the nozzle as above or by a leak-free direct mechanical connection. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Set up the train as in Figure 1, using (if necessary) a very light coat of silicone grease on all ground glass joints, greasing only the outer portion (see APTD-0576) to avoid possibility of contamination by the silicone grease.

Place crushed ice around the impingers.

4.1.4 Leak-Check Procedures.

4.1.4.1 Pretest Leak-Check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, the following procedure shall be used.

After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum.

Note: A lower vacuum may be used, provided that it is not exceeded during the test.

If an asbestos string is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first plugging the inlet to the first impinger and pulling a 380 mm Hg (15 in. Hg) vacuum (see Note immediately above). Then connect the probe to the train and leak-check at about 25 mm Hg (1 in. Hg) vacuum; alternatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 380 mm Hg

(15 in. Hg) vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.02 cfm), whichever is less, are unacceptable.

The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until the desired vacuum is reached. Do not reverse direction of bypass valve; this will cause water to back up into the probe. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak check as shown below and start over.

When the leak-check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable) and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder and silica gel from being entrained backward into the third impinger.

4.1.4.2 Leak-Checks During Sample Run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary, a leak-check shall be conducted immediately before the change is made. The leak-check shall be done according to the procedure outlined in Section 4.1.4.1 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min. (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and plan to correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

Immediately after component changes, leak-checks are optional; if such leak-checks are done, the procedure outlined in Section 4.1.4.1 above shall be used.

4.1.4.3 Post-test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done in accordance with the procedures outlined in Section 4.1.4.1, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3/min. (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and correct sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

4.1.5 Particulate Train Operation. During the sampling run, maintain an isokinetic sampling rate (within 10 percent of true isokinetic unless otherwise specified by the Administrator) and a probe temperature of no greater than 80°C (176°F) temperature as specified by an applicable subpart of the standards or approved by the Administrator.

For each run, record the data required on a data sheet such as the one shown in Figure 2. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted. Take other readings required by Figure 2 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments

in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

Clean the portholes prior to the test run to minimize the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are up to temperature, and that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient is 0.85 $\pm$ 0.02, and the stack gas equivalent density (dry molecular weight) is equal to 29 $\pm$ 4. APTD-0576 details the procedure for using the nomographs. If C_p and M_d are outside the above stated ranges, do not use the nomographs unless appropriate steps (see citation 7 in Section 7) are taken to compensate for the deviations.

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to prevent water from backing inot the probe. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around probe and porthole to prevent unrepresentative dilution of the gas stream.

Traverse the stack cross-section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes; this minimizes the chance of extracting deposited material.

.R _____

TE _____

IN NO. _____

MPLE BOX NO. _____

TER BOX NO. _____

TER ΔH@ _____

ACTOR _____

OT TUBE COEFFICIENT, C_p _____

SCHEMATIC OF STACK CROSS SECTION

BAROMETRIC PRESSURE _____

ASSUMED MOISTURE, % _____

PROBE LENGTH, m (ft) _____

NOZZLE IDENTIFICATION NO. _____

AVERAGE CALIBRATED NOZZLE DIAMETER, cm (in.) _____

PROBE HEATER SETTING _____

LEAK RATE, m^3/min. (cfm) _____

PROBE LINER MATERIAL _____

STATIC PRESSURE, mm Hg (in. Hg) _____

~~FILTER NO.~~ _____

RAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	VACUUM mm Hg (in Hg)	STACK TEMPERATURE (T_S) °C (°F)	VELOCITY HEAD (ΔP_S), mm(in.)H_2O	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER mm H_2O (in. H_2O)	GAS SAMPLE VOLUME m^3 (ft^3)	GAS SAMPLE TEMPERATURE AT DRY GAS METER		FILTER HOLDER TEMPERATURE, °C (°F)	TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °C (°F)
							INLET °C (°F)	OUTLET °C (°F)		
TAL							Avg.	Avg.		
RAGE							Avg.			

Figure 2. Particulate field data.

During the test run, add more ice and, if necessary, salt to maintain a temperature of less than 20°C (68°F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or, in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

Note that when two or more trains are used, separate analyses of the impinger catches from each train shall be performed, unless identical nozzle sizes were used on all trains, in which case, the impinger catches from the individual trains may be combined (as may the impinger catches) and one analysis of impinger catch may be performed. Consult with the Administrator for details concerning the calculation of results when two or more trains are used.

At the end of the sample run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the lamp, record the final dry gas meter reading, and conduct a post-test leak-check, as outlined in Section 4.1.4.3. Also, leak-check the pitot lines as described in Method 2, Section 3.1; the lines must pass this leak-check, in order to validate the velocity head data.

4.1.6 Calculation of Percent Isokinetic. Calculate percent isokinetic (see Calculations, Section 6) to determine whether the run was valid or another test run should be made. If there was difficulty in maintaining isokinetic rates due to source conditions, consult with the Administrator for possible variance on the isokinetic rates.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, thus drawing water from the impingers into the filter holder.

Before moving the sampling train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the impinger inlet where the probe was fastened and cap it. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger or condenser and the probe disconnect the line at the probe and let any condensed water or liquid drain into the impingers or condenser. Either ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

Transfer the probe impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

Save a portion of the water used for cleanup as a blank. Take 200 ml of this water directly from the wash bottle being used and place it in a glass sample container labeled "acetone blank."

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

Container No. 1. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, and probe liner, by washing these components with water and placing the wash in a glass container. Perform the water rinses as follows:

Carefully remove the probe nozzle and clean the inside surface by rinsing with water from a wash bottle and brushing with a Nylon bristle brush. Brush until the water rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse the inside parts of the Swagelok fitting with water in a similar way until no visible particles remain.

Rinse the probe liner with water by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with water. Let the water drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Follow the water rinse with a probe brush. Hold the probe in an inclined position, squirt water into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any water and particulate matter which is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the water or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with water,

and quantitatively collect these washings in the sample container. the brushing, make a final water rinse of the probe as described above.

It is recommended that two people be used to clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

Container No. 2. Measure and record the volume of the first two impingers. Then transfer the contents to a storage container. Rinse the first two impingers and the connecting glassware with water and add the rinse water to the container. Mark the level of the liquid on the container and identify the sample container.

Container No. 3. Measure and record the volume of the third and fourth impingers. Then transfer the contents to a shortage container. Rinse the impinger and connecting glassware with 1.0 N sulfuric acid and add the rinsings to the sample container. Mark the level of liquid on the container and identify the sample container.

Container No. 4. Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for container No. 3 in Section

4.3.

4.3 Analysis. Record the data required on a sheet such as the one shown in Figure 5-3. Handle each sample container as follows:

4.3.1 Container No. 1 and 2. Note the level of liquid in each container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in each container either volumetrically to ± 1 ml or gravimetrically to ± 1.0 g and record on the data sheet. Combine the contents of both containers in a 1 liter volumetric flask and dilute to exactly 1 liter with distilled deionized water. Distill the sample following the procedure in 4.3.5.

4.3.2. Container No. 3. Quantitatively transfer the contents of Container No. 3 to a 1-liter volumetric flask. Rinse the container and cap with several portions of 1.0 N sulfuric acid and transfer to the flask. Dilute to exactly 1 liter with distilled deionized water.

4.3.3 Container No. 4. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

4.3.4 "Water Blank" Container. Measure water in this container either volumetrically or gravimetrically and record on the data sheet. Distill the sample following the rpocedure in 4.3.5.

4.3.5 Sample Distillation.

~~4.3.5.1 Preparation of Equipment. Add 50 ml of distilled deionized water and 20 ml of borate buffer solution to the distillation flask.~~

~~Adjust the pH of the solution to 9.5 with 6 N NaOH using pH paper to measure the pH. Add a few glass beads or boiling chips and heat this mixture until the distillate shows no traces of ammonia as determined with Nessler reagent.~~

4.3.5.~~2~~1 Preparation of Sample. Pipette a 100-ml aliquot of sample into a 500 ml Kjedahl flask or round bottom distillation flask and add 400 ml of distilled deionized water. Add 1 ml of sodium thiosulfate. Then add 25 ml of borate buffer and adjust the pH to 9.5 with 6N NaOH using short-range pH paper to measure the pH. Heat the flask to boiling and boil until the volume is reduced to about 75 ml. Transfer the remaining sample to a 100ml volumetric flask and dilute to exactly 100ml with deionized distilled water.

4.3.5.2 Analysis. ~~deionized, distilled water~~. Pipette 10 ml of this solution into a 25-ml volumetric flask and add 10 ml of the urea color reagent. Dilute to exactly 10 ml with deionized, distilled water. Mix well and allow to stand for at least 10 minutes for full color development. Measure the absorbance of the solution at 420 nm using the blank solution (Section 5.5) as a zero reference. ~~Dilute the sample and the blank with equal amounts of deionized distilled water.~~ If the absorbance exceeds that of the 5.00 mg urea standard, prepare another sample using less than a 10-ml aliquot.

5. Calibration

Maintain a laboratory log of all calibrations.

5.1 Probe Nozzle. Probe nozzles shall be calibrated before their

initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

5.2 Pitot Tube. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of Method 2.

5.3 Metering System. Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry gas meter dial readings to correspond to the wet test meter readings, calibration factors may be used to mathematically correct the gas meter dial readings to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases, the following leak-check procedure is suggested: make a 10-minute calibration run at 0.00057 m^3/min (0.02 cfm); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by 10, to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 cfm).

After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate orifice setting (based on the previous field test), with the vacuum set at the maximum value reached during the test series.

the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

Alternative procedures, e.g., using the orifice meter coefficients, may be used, subject to the approval of the Administrator.

Note: If the dry gas meter coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

5.4 Probe Heater Calibration. The probe heating system shall be calibrated before its initial use in the field according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

5.5 Temperature Gauges. Use the procedure in Section 4.3 of Method 2 to calibrate in-stack temperature gauges. Dial thermometers, such as are used for the dry gas meter and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

5.6 Leak Check of Metering System Shown in Figure 5-1. That portion of the sampling train from the pump to the orifice meter should be leak checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 5-4): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber

tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

5.7 Barometer. Calibrate against a mercury barometer.

5.8 Determination of Spectrophotometer Calibration Factor K.

5.8.1 Urea Analysis. Add 0.0, 1.0, 2.0, 3.0, and 4.0 ml of working standard urea solution to a series of five 25-ml volumetric flasks. Pipette 10 ml of the urea color reagent into the flask and dilute to exactly 25 ml with deionized distilled water. Mix well and allow each to stand for at least 10 minutes for color development. Measure the absorbance of each standard at 420 nm. The calibration procedure must be repeated each day that samples are analyzed. Calculate the spectrophotometer calibration factor as follows:

$$K_{cu} = 1250 \cdot \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2 + A_5^2}$$

Where:

K_{cu} = Calibration factor for urea analysis.

A_1 = Absorbance of the 1250 μg standard

A_2 = Absorbance of the 2500 μg standard.

A_3 = Absorbance of the 3750 μg standard.

A_4 = Absorbance of the 5000 μg standard.

5.8.2 Ammonia Analysis: Add 0.0, 1.0, 2.0, 5.0, 8.0, and 10.0 ml of working standard ammonium chloride solution to a series of six 25-ml volumetric flasks. Adjust the total volume of solution in each

to 20 ml using 1.0 N H_2SO_4. Adding 10 N NaOH dropwise, adjust the pH to between 8 and 10. Pipette exactly 0.5 ml of Nessler reagent into each flask and dilute to exactly 25 ml with deionized distilled water. Mix well and allow each to stand for 10 to 30 minutes for color development. Note the time allowed for color development of the standards and use the same time for the samples. Measure the absorbance of each standard at 405 nm. The calibration procedure must be repeated each day that samples are analyzed. Calculate the spectrophotometer calibration factor as follows:

$$K_{cA_3} = 10 \frac{A_1 + 2A_2 + 5A_3 + 8A_4 + 10A_5}{A_1^2 + A_2^2 + A_3^2 + A_4^2 + A_5^2}$$

Where:

K_{cA} = Calibration factor.

A_1 = Absorbance of the 10 μg standard.

A_2 = Absorbance of the 20 μg standard.

A_3 = Absorbance of the 50 μg standard.

A_4 = Absorbance of the 80 μg standard.

A_5 = Absorbance of the 100 μg standard.

6. Calculation

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

6.1 Nomenclature.

A = Absorbance of sample.

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_a = Acetone blank residue concentration, mg/g.

$C\ NH_3$ = Concentration of ammonia, dry basis corrected to standard condition, mg/dscm (lb/dscf).

c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).

C_u = Concentration of urea, dry basis corrected to standard condition, mg/dscm (lb/dscf).

F_a = Dilution factor (i.e., 25/5, 25/10, etc.) required only if sample dilution was needed to reduce the absorbance into the range of calibration.

I = Percent of isokinetic sampling.

$K_{c\ NH_3}$ = Spectrophotometer calibration factor, ammonia analysis.

K_u = Spectrophotometer calibration factor, urea analysis.

L_a = Maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change; equal to 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

L_i = Individual leakage rate observed during the leak check conducted prior to the "i^{th}" component change (i = 1, 2, 3...n), m^3/min (cfm).

L_p = Leakage rate observed during the post-test leak check, m^3/min (cfm).

M_a = Mass of residue of acetone after evaporation.

M_n = Total amount of particulate matter collected, mg.

M_{NH_3} = Mass of ammonia in gas sample μg.

M_u = Mass of urea in gas sample, μg.

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3/°K-g-mole (21.85 in. Hg-ft^3/°R-lb-mole).

T_m = Absolute average dry gas meter temperature (see Figure 5-2), °K(°R).

T_s = Absolute average stack gas temperature (see Figure 5-2), °K (°R).

T_{std} = Standard absolute temperature, 293°K (528°R).

V_a = Volume of acetone blank, ml.

V_{al} = Volume of sample aliquot, analyzed, ml.

V_{aw} = Volume of acetone used in wash, ml.

V_{lc} = Total volume of liquid collected in impingers and silica gel (see Figure 5-3), ml.

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

V_{soln} = Total volume of solution in which the sample is contained, ml.

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

v_s = Stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (ft/sec).

W_a = Weight of residue in acetone wash, mg.

Y = Dry gas meter calibration factor.

ΔH = Average pressure differential across the orifice meter (see Figure 5-2), mm H_2O (in. H_2O).

ρ_a = Density of acetone, mg/ml (see label on bottle).

ρ_W = Density of water, 0.9982 g/ml (0.002201 lb/ml).

θ = Total sampling time, min.

θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.

θ_i = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.

θ_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

6.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 5-2).

6.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20°C, 760 mm Hg or 68°F, 29.92 in. Hg) by using Equation -1.

$$V_{m(std)} = V_m Y \frac{T_{std}}{T_m} \frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} = K_1 V_m Y \frac{P_{bar} + (\Delta H/13.6)}{T_m}$$

Equation -1.

Where:

K_1 = 0.3858 °K/mm Hg for metric units

= 17.64 °R/in. Hg for English units

Note: Equation -1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (i.e., the post-test leak check or leak checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation -1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation -1 with the expression:

$$[V_m - (L_p - L_a)\,\theta]$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m in Equation 5-1 by the expression:

$$[V_m - (L_1 - L_a)\,\theta_1 - \sum_{i=2}^{n} (L_i - L_a)\,\theta_i - (L_p - L_a)\,\theta_p]$$

and substitute only for those leakage rates (L_i or L_p) which exceed L_a.

6.4 Volume of water vapor.

$$V_{w(std)} = V_{1c}\left(\frac{\rho_w}{M_w}\right)\left(\frac{RT_{std}}{P_{std}}\right) = K_2\,V_{1c} \qquad \text{Equation 5-2}$$

where:

K_2 = 0.001333 m^3/ml for metric units

= 0.04707 ft^3/ml for English units.

6.5 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Equation 5-3}$$

Note: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 5-3), and a second from the assumption of saturated conditions. The lower of the two values of B_{ws} shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the Note of Section 1.2 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 5-2 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is $\pm$ 1°C (2°F).

6.6 Acetone Blank Concentration.

$$C_a = \frac{m_a}{V_a \rho_a}$$

6.7 Acetone Wash Blank.

$$W_a = C_a V_{aw} \rho_a$$

6.8 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from containers 1 and 2 less the acetone blank (see Figure 5-3). Note: Refer to Section 4.1.5 to assist in calculation of results involving two or more filter assemblies or two or more sampling trains.

6.9 Particulate Concentration.

$$C_s = (0.001\ g/mg)\ (M_a/V_{m(std)}) \qquad \text{Equation 6}$$

6.10 Total Mass of Urea Per Sample.

$$M_u = K_{cu}\ AF\ \frac{V_{al}}{V_{Soln}} \qquad \text{Equation 7}$$

6.11 Urea Concentration.

$$C_u = K_2\ \frac{M_u}{V_{sc}} \qquad \text{Equation 8}$$

Where:

$K_2 = 10^3\ \frac{Mg/m^3}{\mu g/ml}$ for metric units.

$6.243 \times 10^{-5}\ \frac{lb/SCF}{\mu g/ml}$ for English units.

6.12 Total Mass of NH_3 Per Sample.

$$M_{NH_3} = K_{C\ NH_3}\ AF\ \frac{V_{al}}{V_{Soln}} \qquad \text{Equation 9}$$

6.13 Ammonia Concentration.

$$C_{NH_3} = K_2\ \frac{M}{V_{sc}} \qquad \text{Equation 10}$$

Where: $K_2 = 10^3\ \frac{mg/m^3}{\mu g/ml}$ for Metric units.

$= 6.243 \times 10^{-5}\ \frac{lb/SCF}{\mu g/ml}$ for English units.

6.14 Conversion Factors:

From	To	Multiply by
scf	m^3	0.02832
g/ft^3	gr/ft^3	15.43
g/ft^3	lb/ft^3	2.205×10^{-3}
g/ft^3	g/m^3	35.31

6.15 Isokinetic Variation.

6.15.1 Calculation From Raw Data.

$$I = \frac{100\ T_s\ [K_3\ V_{1c} + (V_m\ Y/T_m)\ \ (P_{bar} + \Delta H/13.6)]}{60\ \ \theta\ \ v_s\ P_s\ A_n}$$

Equation 11

where:

K_3 = 0.003454 mm Hg-m^3/ml-°K for metric units

= 0.002669 in. Hg-ft^3/ml-°R for English units.

6.15.2 Calculation From Intermediate Values.

$$I = \frac{T_s\ V_{m(std)}\ P_{std}\ 100}{T_{std}\ v_s\ \theta\ A_n\ P_s\ 60\ (1-B_{ws})}$$

$$= K_4\ \frac{T_s\ V_{m(std)}}{P_s\ v_s\ A_n\ \theta\ (1-B_{ws})}$$

Equation 12

where:

K_4 = 4.320 for metric units

= 0.09450 for English units.

6.16 Acceptable Results. If 90 percent $\leq$ I $\leq$ 110 percent, the results are acceptable. If the results are low in comparison to the standard and I is beyond the acceptable range, or, if I is less than 90 percent, the Administrator may opt to accept the results. Use Citation 4 to make judgments. Otherwise, reject the results and repeat the test.

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APPENDIX A.3

MODIFIED PROCEDURE - JANUARY 1980

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DETERMINATION OF PARTICULATE, AND UREA EMISSIONS FROM UREA PLANTS

1. Principle and Applicability

1.1 Principle. A gas sample is extracted isokinetically from the stack. The ammonia is removed from the sample by boiling, and the urea is measured by a colorimetric procedure.

1.2 Applicability. This method is applicable for the determination of urea from urea manufacturing facilities.

2. Apparatus

2.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 1; it is similar to construction to Method 5. The sampling train consists of the following components.

2.1.1 Probe Nozzle, Probe Liner, Pitot Tube, Differential Pressure Gauge, Metering System, and Barometer. Same as Method 5, sections 2.1.1, 2.1.2, 2.1.3, 2.1.4, 2.1.8, and 2.1.9 respectively. Stainless steel probe liners may also be used.

2.1.2 Impingers--Five as shown in Figure 1. The second and third shall be of the Greenburg-Smith design with standard tips. The first, fourth, and fifth shall be of the Greenburg-Smith design, modified by replacing the insert with an approximately 13 millimeter (0.5 in) I.D. glass tube, having an unconstricted tip located 13 mm (0.5 in) from the bottom of the flask. Similar collection systems, which have been approved by the Administrator, may be used.

2.2 Sample Recovery. The following equipment is needed:

2.2.1 Probe-Liner and Probe-Nozzle Brushes, Graduated Cylinder and/or Balance, Plastic Storage Container, and Rubber Policeman. Same as Method 5, sections 2.2.1, 2.2.5, 2.2.6, 2.2.7, respectively.

2.2.2 Wash Bottles--Two. Glass wash bottles are recommended; polyethylene wash bottles may be used at the option of the tester.

2.2.3 Glass or Plastic Sample Storage Containers. Chemically resistant, borosilicate glass bottles 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free. (Narrow mouth glass bottles have been found to be less prone to leakage). Alternatively, polyethylene bottles may be used.

2.2.4 Funnel, Glass or Polypropylene.

2.3 Analysis.

2.3.1 Pipettes. Volumetric type 0.5-ml, 2-ml, 5-ml, 8-ml, 10-ml, 20-ml, and 25-ml sizes.

2.3.2 Volumetric Flasks. 25-ml size, 100-ml size, 250-ml size, 500-ml size and 1000-ml size.

2.3.3 Graduated Cylinder. 100-ml size.

2.3.4 Distillation Apparatus.

2.3.4.1 Flasks or Beakers. At least two, 800-ml size.

2.3.4.2 Hot Plate. Capable of heating the distillation flasks to 120°C (248°F).

2.3.5 Spectrophotometer. To measure absorbance at 420 nanometers.

2.3.6 Sample Cells. Two matched absorbance cells to fit the spectrophotometer.

3. Reagents

Use ACS reagent-grade chemicals or equivalent, unless otherwise specified. The reagents used in sampling and sample recovery are as follows:

3.1 Sampling and Sample Recovery.

3.1.1 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, sections 3.1.2, 3.1.4, 3.1.5, respectively.

3.1.2 Water. Deionized distilled to conform to ASTM specification D 1193-74, type 3. At the option of the analyst, the $KMNO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.1.3 Sulfuric Acid, 1 N. Dilute 28 ml of concentrated sulfuric acid to 1 liter with deionized distilled water.

3.2 Analysis. The reagents need for analysis are listed below.

3.2.1 Water. Same as 3.1.2.

3.2.2 Sodium Hydroxide (NaOH), 10 N. Dissolve 40 g of NaOH in a 100-ml volumetric flask and dilute to exactly 100 ml with deionized distilled water.

3.2.3 Sodium Hydroxide 6 N. Dissolve 240 g of NaOH in 800 ml of deionized distilled water in a 1-liter flask. Dilute to exactly 1 liter with deionized distilled water.

3.2.4 Sodium Hydroxide 1 N. Dissolve 40 g of NaOH in 800 ml of deionized distilled water in a 1-liter flask and dilute to exactly 1 liter with deionized distilled water.

3.2.5 Sodium Hydroxide 0.1 N. Dilute 100 ml of 1 N NaOH to exactly 1 liter with deionized distilled water.

3.2.6 Borate Buffer. Dissolve 2.5 g of sodium tetraborate, $Na_2B_4O_7$, or 4.8 g of the decahydrate $Na_2B_4O_7 \cdot 10\ H_2O$, in 500 ml of deionized distilled water in a 1-liter volumetric flask. Add 88 ml of 0.1 N NaOH solution and dilute to exactly 1 liter with deionized distilled water.

3.3.7 Sulfuric Acid 1 N. Slowly add 28 ml of concentrated sulfuric acid to 800 ml of deionized distilled water in a 1-liter flask and dilute to exactly 1 liter with deionized distilled water.

3.3.8 Ethyl Alcohol, 95 percent.

3.3.9 P-dimethylaminobenzaldehyde.

3.3.10 Hydrochloric Acid, Concentrated (36.5 - 38 percent by weight).

3.3.11 Stock Standard Urea Solution. Dissolve 5.000 g of urea in 500 ml of deionized distilled water in a 1-liter flask and dilute to exactly 1 liter with deionized distilled water.

3.3.12 Urea Color Reagent. Prepare the color reagent by dissolving 2.000 g of P-dimethylaminobenzaldehyde in a mixture of 100 ml of 95 percent ethyl alcohol and 10 ml of hydrochloric acid.

4. Procedure

4.1 Sampling. Because of the complexity of this method, testers should be trained and experienced with the test procedure to insure reliable results.

4.1.1 Pretest Preparation. Follow the general procedure given in Method 5, section 4.1.1, except omit the directions for the filter.

4.1.2 Preliminary Determinations. Follow the general procedure given in Method 5, section 4.1.2.

4.1.3 Preparation of Sampling Train. Follow the general procedure given in Method 5, section 4.1.3, except place 100 ml of deionized distilled water in each of the first two impingers, place 100 ml of 1 N H_2SO_4 in the third impinger, leave the fourth impinger empty, and place the preweighed silica gel in the fifth impinger. Assemble the train as shown in Figure 1.

4.1.4 Leak Check Procedures. Follow the leak-check procedures given in Method 5, sections 4.1.4.1 (Pretest Leak Check), 4.1.4.2 (Leak-Check During Sampling Run) and 4.1.4.3 (Post-Test Leak-Check).

4.1.5 Sampling Training Operation. Follow the general procedure given in Method 5, section 4.1.5. For each run, record the data required on a data sheet such as the one shown in Method 5, Figure 5-2.

4.1.6 Calculation of Percent Isokinetic. Same as Method 5, section 4.1.6.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, thus drawing water from the impingers into the filter holder.

Before moving the sampling train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the impinger inlet where the probe was fastened and cap it. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger or condenser and the probe, disconnect the line at the probe and let any condensed water or liquid drain into the impingers or condenser. Either ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

Transfer the probe-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

Save a portion of the deionized distilled water used for cleanup as a blank. Take 200 ml of this water directly from the wash bottle being used and place it in a glass sample container labeled "water blank."

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

Container No. 1. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, and probe liner, by washing these components with water and placing the wash in a glass container. Perform the water rinses as follows:

Carefully remove the probe nozzle and clean the inside surface by rinsing with water from a wash bottle and brushing with a Nylon bristle brush. Brush until the water rinse shows no visible particles, after which make a final rinse of the inside surface with water.

Brush and rinse the inside parts of the Swagelok fitting with water in a similar way until no visible particles remain.

Rinse the probe liner with water by tilting and rotating the probe while squirting water into its upper end so that all inside surfaces will be wetted with water. Let the water drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Follow the water rinse with a probe brush. Hold the probe in an inclined position, squirt water into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any water and particulate matter which is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the water or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with water, and quantitatively collect these washings in the sample container. After brushing, make a final water rinse of the probe as described above.

It is recommended that two people be used to clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

Container No. 2. Measure and record the volume of the first two impingers. Then transfer the contents to the container. Rinse the first two impingers and the connecting glassware with water and add the rinse water to the container. Mark the level of the liquid on the container and identify the sample container.

Impingers Nos. 3 and 4. Measure and record the volume of the third and fourth impingers. Discard the liquid.

Container No. 3. Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fifth impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for container No. 3 in section 4.3.

4.3 Analysis. Record the data required on a sheet such as the one shown in Figure 5-3. Handle each sample container as follows:

4.3.1 Container Nos. 1 and 2. Note the level of liquid and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid either volumetrically to ± 1 ml or gravimetrically to ± 1.0 g and record on the data sheet. Combine the contents of both containers in a 500-ml volumetric flask and dilute to exactly 500 ml with deionized distilled water. Distill the sample following the procedure in 4.3.4.

4.3.2 Container No. 3. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

4.3.3 "Water Blank" Container. Measure water in this container either volumetrically or gravimetrically and record on the data sheet. Distill the sample following the procedure in 4.3.4.

4.3.4 Sample Distillation. Treat the combined sample 1 and 2 and the water blank as follows:

4.3.4.1 Preparation of Sample. Pipette a 100-ml aliquot of sample into a 1-liter flask or beaker and add 400 ml of deionized distilled water. Then add 25 ml of borate buffer and adjust the pH to 9.5 with 6N NaOH using short-range pH paper to measure the pH. Heat the flask to boiling and boil until the volume is reduced to about 75 ml. (Caution: This step should be conducted under a hood.) Transfer the remaining sample to a

100-ml volumetric flask and dilute to exactly 100 ml with deionized distilled water.

4.3.4.2 Analysis. Pipette 10 ml of this solution into a 25-ml volumetric flask and add 10 ml of the urea color reagent. Dilute to exactly 25 ml with deionized distilled water. Mix well and allow to stand for at least 10 minutes for full color development. Measure the absorbance of the solution at 420 nm using the blank solution (section 5.5) as a zero reference. If the absorbance exceeds that of the 5.00 mg urea standard, prepare another sample using less than a 10-ml aliquot.

5. Calibrations

5.1 Sampling Train. Calibrate the sampling train components according to the indicated section of Method 5. Probe Nozzle (5.1); Pitot Tube (5.2); Metering System (5.3); Temperature Gauge (5.5); Leak-Check of the Metering System (5.6); and Barometer (5.7).

5.2 Determination of Spectrophotometer Calibration Factor K. Add 0.0, 5.0, 10.0, 15.0, 20.0 and 25.0 ml of the stock standard urea solution to a series of six 250-ml volumetric flasks. Then follow the distillation and analysis procedures described for the samples in section 4.3.4 of this method. Each standard at the time of analysis will contain 0, 1.00, 2.00, 3.00, 4.00, and 5.00 mg respectively. The calibration procedure must be repeated each day that samples are analyzed. Calculate the spectrophotometer calibration factor as follows:

$$K_c = 1.00 \frac{A_1 + 2A_2 + 3A_3 + 4A_4 + 5A_5}{A_1^2 + A_2^2 + A_3^2 + A_4^2 + A_5^2}$$

Where:

K_c = Calibration factor.

A_1 = Absorbance of the 1.00 mg standard.

A_2 = Absorbance of the 2.00 mg standard.

A_3 = Absorbance of the 3.00 mg standard.

A_4 = Absorbance of the 4.00 mg standard.

A_5 = Absorbance of the 5.00 mg standard.

6. Calculations

6.1 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop, Dry Gas Volume, Volume of Water Vapor, Moisture Content, Isokinetic Variation, and Acceptable Results. Using data from this test, same as Method 5, sections 6.2, 6.3, 6.4, 6.5, 6.11, and 6.12 respectively.

6.2 Mass of Urea. Calculate the total weight of urea collected in the sample by Equation 1.

$$M = K_c \left(A_s \frac{V_{soln}}{V_{al}} - A_w \frac{V_w}{V_b}\right) \qquad \text{Eq. 1.}$$

Where:

M = Mass of urea collected, mg.

K_c = Spectrophotometer calibration factor.

A_s = Absorbance of sample.

A_w = Absorbance of the water blank

V_{al} = Volume of sample aliquot analyzed, ml.

V_b = Volume of water-blank aliquot analyzed, ml.

V_{soln} = Total volume of solution in which the sample is contained, ml.

V_w = Volume of sample returned for analysis, ml.

6.3 Particulate Concentration: Calculate the particulate (urea) concentration as follows:

$$c = K_2 \frac{M}{V_{m(std)}} 10^{-6} \qquad \text{Eq. 2}$$

Where:

c = Particulate (urea) concentration at dry standard conditions, g/dscm (gr/dscf).

M = Mass of urea collected, g.

$V_{m(std)}$ = Volume of gas sample measured by dry gas meter, corrected to standard conditions, dscm (dscf).

K = 1.0 for metric units.

= 0.4370 for English units.

7. Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 13th Edition. American Public Health Association, Washington, D.C., pp. 226-232, 1974.

2. Watt, George W. and Joseph D. Chrisp. Spectrophotometric Method for Determination of Urea. Analytical Chemistry. 26:452-453, 1954.

3. Same as Method 5, Citation/through 9 of section 7.

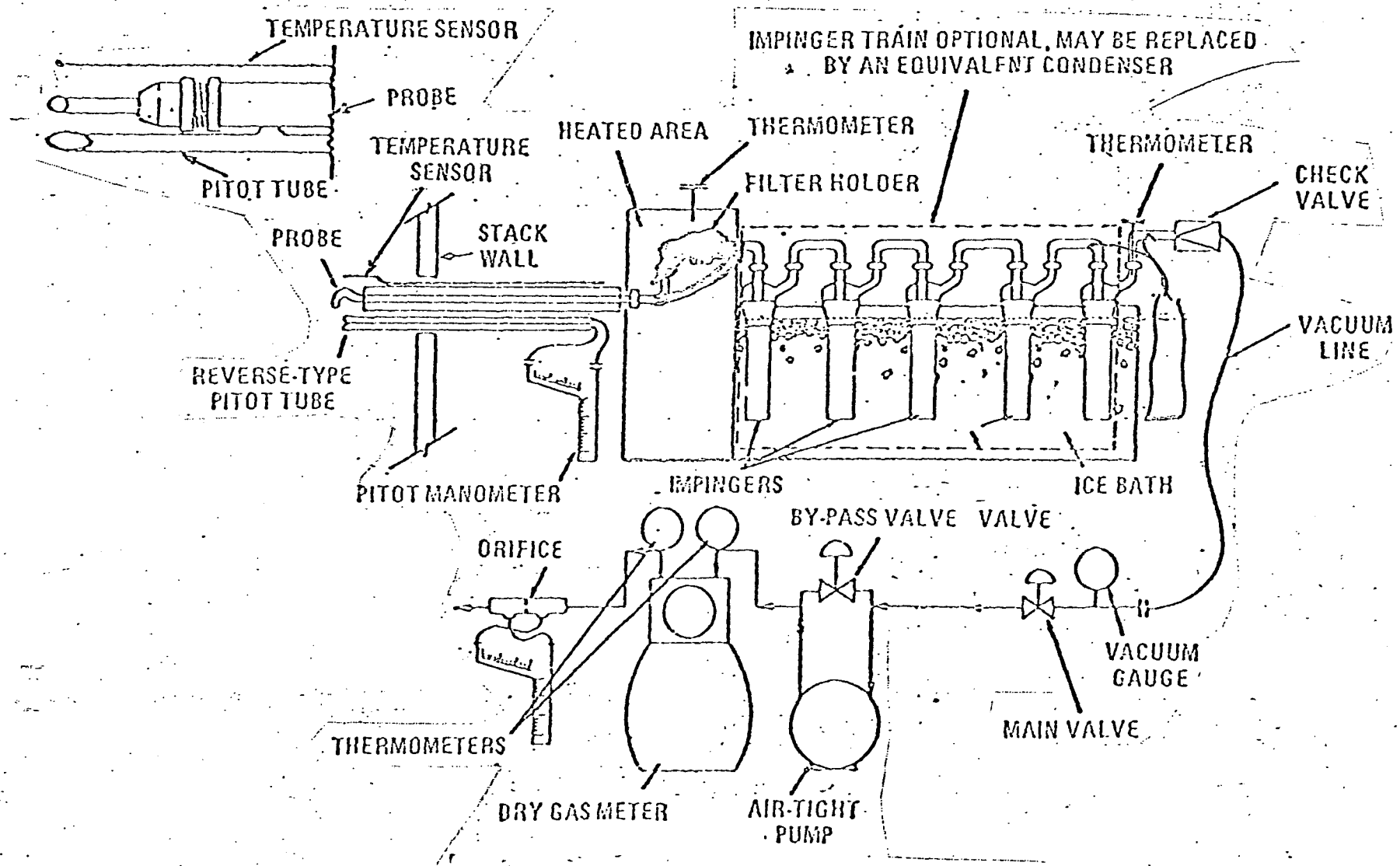

Figure 1. Particulate sampling train

APPENDIX A.4

PROPOSED REFERENCE METHOD 28

5/12/80

APPENDIX A - REFERENCE TEST METHOD

* * * * *

METHOD 28 - DETERMINATION OF PARTICULATE (UREA) EMISSIONS FROM UREA PLANTS

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of particulate emissions as urea from urea manufacturing facilities.

1.2 Principle. A gas sample is extracted isokinetically from the stack. The ammonia is removed from the sample by boiling, and the particulate emissions are determined as urea by a colorimetric procedure.

2. Apparatus

2.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 28-1; it is similar in construction to Method 5. The sampling train consists of the following components.

2.1.1 Probe Nozzle, Probe Liner, Pitot Tube, Differential Pressure Gauge, Metering System, and Barometer. Same as Method 5, sections 2.1.1, 2.1.2, 2.1.3, 2.1.4, 2.1.8, and 2.1.9 respectively. Stainless steel probe liners may also be used.

2.1.2 Impingers. Five impingers connected in series as shown in Figure 28-1. For the second and third impinger, the tester shall use the Greenburg-Smith design with standard tips. For the first, fourth, and fifth impingers, the tester may use the Greenburg-Smith design, modified by replacing the tips with a 1.25 cm (0.5 in.) ID

glass tube extending to 1.25 cm (0.5 in.) from the bottom of the flask. Similar collection systems, which have been approved by the Administrator, may be used.

2.2 Sample Recovery. The following equipment is needed:

2.2.1 Probe-Liner and Probe-Nozzle Brushes, Graduated Cylinder and/or Balance, Plastic Storage Containers, and Rubber Policeman. Same as Method 5, sections 2.2.1, 2.2.5, 2.2.6, 2.2.7, respectively.

2.2.2 Wash Bottles. Glass wash bottles are recommended; polyethylene wash bottles may be used at the option of the tester.

2.2.3 Sample Storage Containers. Chemically resistant, borosilicate glass bottles, 500-ml or 1000-ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free. (Narrow mouth glass bottles have been found to be less prone to leakage). Alternatively, polyethylene bottles may be used.

2.2.4 Funnel. Glass or Polyethylene.

2.3 Analysis. For analysis, the following equipment is needed.

2.3.1 Pipettes. Volumetric type, 0.5-ml, 2-ml, 5-ml, 8-ml, 10-ml, 20-ml, and 25-ml.

2.3.2 Volumetric Flasks. 25-ml, 100-ml, 250-ml, 500-ml, and 1000-ml.

2.3.3 Graduated Cylinder. 100-ml.

2.3.4 Distillation Apparatus.

2.3.4.1 Flasks or Beakers. At least two, 800-ml.

2.3.4.2 Hot Plate. Capable of heating the distillation flasks to 120°C (248°F).

2.3.5 Spectrophotometer. To measure absorbance at 420 nanometers.

2.3.6 Sample Cells. Two matched absorbance cells to fit the spectrophotometer.

3. Reagents

Use ACS reagent-grade chemicals or equivalent, unless otherwise specified.

3.1 Sampling and Sample Recovery. The reagents used in sampling and sample recovery are as follows:

3.1.1 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, sections 3.1.2, 3.1.4, 3.1.5, respectively.

3.1.2 Water. Deionized distilled to conform to ASTM specification D 1193-74, type 3. At the option of the analyst, the $KMNO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.1.3 Sulfuric Acid, 1 N. Slowly add 28 ml of concentrated sulfuric acid to 800 ml of deionized distilled water in a 1-liter flask and dilute to exactly 1 liter with deionized distilled water.

3.2 Analysis. The reagents need for analysis are listed below:

3.2.1 Water. Same as 3.1.2.

3.2.2 Sodium Hydroxide (NaOH), 10 N. Dissolve 40 g of NaOH in a 100-ml volumetric flask and dilute to exactly 100 ml with deionized distilled water.

3.2.3 Sodium Hydroxide 6 N. Dissolve 240 g of NaOH in 800 ml of deionized distilled water in a 1-liter flask. Dilute to exactly 1 liter with deionized distilled water.

3.2.4 Sodium Hydroxide, 1 N. Dissolve 40 g of NaOH in 800 ml of deionized distilled water in a 1-liter flask and dilute to exactly 1 liter with deionized distilled water.

3.2.5 Sodium Hydroxide, 0.1 N. Dilute 100 ml of 1 N NaOH to exactly 1 liter with deionized distilled water.

3.2.6 Borate Buffer. Dissolve 2.5 g of sodium tetraborate ($Na_2B_4O_7$) or 4.8 g of the decahydrate ($Na_2B_4O_7 \cdot 10\ H_2O$) in 500 ml of deionized distilled water in a 1-liter volumetric flask. Add 88 ml of 0.1 N NaOH solution, and dilute to exactly 1 liter with deionized distilled water.

3.3.7 Sulfuric Acid, 1 N. Same as 3.1.3.

3.3.8 Ethyl Alcohol, 95 percent.

3.3.9 P-dimethylaminobenzaldehyde.

3.3.10 Hydrochloric Acid, Concentrated.

3.3.11 Urea Solution, 2.5 mg/ml. Dissolve 2.500 g of urea in 500 ml of deionized distilled water in a 1-liter flask and dilute to exactly 1 liter with deionized distilled water.

3.3.12 Urea Color Reagent. Dissolve 2.000 g of p-dimethylaminobenzaldehyde in a mixture of 100 ml of 95 percent ethyl alcohol and 10 ml of concentrated hydrochloric acid.

4. Procedure

4.1 Sampling. Because of the complexity of this method, testers should be trained and experienced with the test procedure to insure reliable results.

4.1.1 Pretest Preparation. Follow the general procedure given in Method 5, section 4.1.1, except omit the directions for the filter.

4.1.2 Preliminary Determinations. Follow the general procedure given in Method 5, section 4.1.2.

4.1.3 Preparation of Sampling Train. Follow the general procedure given in Method 5, section 4.1.3, except place 100 ml of deionized distilled water in each of the first three impingers, place 100 ml of 1 N H_2SO_4 in the fourth impinger, and place the preweighed silica gel in the fifth impinger. Assemble the train as shown in Figure 28-1.

4.1.4 Leak Check Procedures. Follow the leak-check procedures given in Method 5, sections 4.1.4.1 (Pretest Leak Check), 4.1.4.2 (Leak-Check During Sampling Run) and 4.1.4.3 (Post-Test Leak-Check).

4.1.5 Sampling Training Operation. Follow the general procedure given in Method 5, section 4.1.5. For each run, record the data required on a data sheet such as the one shown in Method 5, Figure 5-2.

4.1.6 Calculation of Percent Isokinetic. Same as Method 5, section 4.1.6.

4.2 Sample Recovery. Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle, and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum, thus drawing water from the impingers into the probe.

Before moving the sampling train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the impinger inlet where the probe was fastened and cap it. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger or condenser and the probe, disconnect the line at the probe and let any condensed water or liquid drain into the impingers or condenser. Either ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

Transfer the probe-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

4.2.1 Container No. 1. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, and probe liner, by washing

these components with water and placing the wash in a glass container. Perform the water rinses as follows:

Carefully remove the probe nozzle and clean the inside surface by rinsing with water from a wash bottle and brushing with a Nylon bristle brush. Brush until the water rinse shows no visible particles, after which make a final rinse of the inside surface with water.

Brush and rinse the inside parts of the Swagelok fitting with water in a similar way until no visible particles remain.

Rinse the probe liner with water by tilting and rotating the probe while squirting water into its upper end so that all inside surfaces will be wetted with water. Let the water drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Follow the water rinse with a probe brush. Hold the probe in an inclined position, squirt water into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any water and particulate matter which is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the water or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped.

Rinse the brush with water, and quantitatively collect these washings in the sample container. After brushing, make a final water rinse of the probe as described above.

It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

4.2.2 Container No. 2. Mark the liquid level of the container to determine later if leakage occurred during shipment. Cap and seal the containers and identify. Measure to the nearest ± 1 ml and record the volume of the first three impingers. Then transfer the contents to the container. Rinse the first three impingers and the connecting glassware with water, and add the rinse water to the container. Mark the level of the liquid on the container and identify the sample container.

4.2.3 Impinger No. 4. Measure to the nearest ± 1 ml and record the volume of the fourth impinger. Discard the liquid.

4.2.4 Container No. 3. Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fifth impinger to its original container and seal. The tester may use a funnel and rubber policeman as aids in transferring the silica gel. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance

is available in the field, the tester may follow the procedure for container No. 3 in section 4.3.2.

4.2.5 Water Blank. Save a portion of the deionized distilled water used for cleanup as a blank. Take 200 ml of this water directly from the wash bottle being used and place it in a glass sample container labeled "water blank."

4.3 Analysis. Record the data required on a sheet such as the one shown in Figure 5-3 of Method 5. Handle each sample container as follows:

4.3.1 Containers No. 1 and 2. Note the level of liquid and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid either volumetrically to ± 1 ml or gravimetrically to ± 0.5 g, and record on the data sheet. Combine the contents of both containers in a 500-ml volumetric flask, and dilute to exactly 500 ml with deionized distilled water. Distill the sample following the procedure in 4.3.4.

4.3.2 Container No. 3. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

4.3.3 "Water Blank" Container. Measure water in this container either volumetrically or gravimetrically and record on the data sheet. Distill the sample following the procedure in 4.3.4.

4.3.4.1 Preparation of Sample. Pipette a 100-ml aliquot of sample into a 1-liter flask or beaker, and add 400 ml of deionized distilled water. Then add 25 ml of borate buffer, and adjust the pH to 9.5 with 6N NaOH using short-range pH paper to measure the pH. Heat the flask to boiling and boil until the volume is reduced to about 75 ml. (Caution: Conduct this step under a hood.) Transfer the remaining sample to a 100-ml volumetric flask and dilute to exactly 100 ml with deionized distilled water.

4.3.4.2 Analysis. Treat the sample and blank as follows: Pipette 10 ml into a 25-ml volumetric flask and add 10 ml of the urea color reagent. Dilute to exactly 25 ml with deionized distilled water. Mix well and allow to stand for at least 10 minutes for full color development. Measure the absorbance of the solution of 420 nm using the blank solution as a zero reference. If the absorbance exceeds that of the 5.00-μg/ml urea standard, prepare another sample using less than a 10-ml aliquot.

5. Calibrations

5.1 Sampling Train. Calibrate the sampling train components according to the indicated section of Method 5. Probe Nozzle (5.1);

Pitot Tube (5.2); Metering System (5.3); Temperature Gauge (5.5); Leak-Check of the Metering System (5.6); and Barometer (5.7).

5.2 Determination of Spectrophotometer Calibration Factor K. Add 0.0, 1.0, 5.0, 10.0, 15.0, 20.0 and 25.0 ml of the standard urea solution to a series of six 250-ml volumetric flasks. Then follow the distillation and analysis procedures described for the samples in section 4.3.4 of this method. Each standard at the time of analysis will contain 0, 0.100, 0.500, 1.00, 1.50, 2.00, and 2.50 mg respectively. The calibration procedure must be repeated each day that samples are analyzed. Calculate the spectrophotometer calibration factor as follows:

$$K_c = 0.100 \frac{A_1 + 5A_2 + 10A_3 + 15A_4 + 20A_5 + 25A_6}{A_1^2 + A_2^2 + A_3^2 + A_4^2 + A_5^2 + A_6^2}$$

Where:

K_c = Calibration factor.

A_1 = Absorbance of the 0.100 mg standard.

A_2 = Absorbance of the 0.500 mg standard.

A_3 = Absorbance of the 1.00 mg standard.

A_4 = Absorbance of the 1.50 mg standard.

A_5 = Absorbance of the 2.0 mg standard.

A_6 = Absorbance of the 2.50 mg standard.

6. Calculations

6.1 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop, Dry Gas Volume, Volume of Water Vapor, Moisture Content, Isokinetic Variation, and Acceptable Results. Using data from this test, same as Method 5, sections 6.2, 6.3, 6.4, 6.5, 6.11, and 6.12 respectively.

6.2 Mass of Urea. Calculate the total weight of urea collected in the sample by Equation 28-1.

$$m = K_c \left(A_s \frac{V_{soln}}{V_{al}} - A_w \frac{V_w}{V_b}\right) \qquad \text{Eq. 28-1}$$

Where:

m = Mass of urea collected, mg.

K_c = Spectrophotometer calibration factor.

A_s = Absorbance of sample.

A_w = Absorbance of the water blank.

V_{al} = Volume of sample aliquot analyzed, ml.

V_{soln} = Total volume of solution in which the sample is contained, ml.

6.3 Particulate Concentration: Calculate the particulate (urea) concentration as follows:

$$c = K_2 \frac{m}{V_{m(std)}} 10^{-3} \qquad \text{Eq. 28-2}$$

Where:

c = Particulate (urea) concentration at dry standard conditions, g/dscm (gr/dscf).

m = Mass of urea collected, g.

$V_{m(std)}$ = Volume of gas sample measured by dry gas meter, corrected to standard conditions, dscm (dscf).

K_2 = 1.0 for metric units.

= 0.4370 for English units.

7. Bibliography

1. American Public Health Association. Standards Methods for the Examination of Water and Wastewater, 13th Edition. Washington, D.C. 1974. pp. 226-232.

2. Watt, George W. and Joseph D. Chrisp. Spectrophotometric Method for Determination of Urea. Analytical Chemistry. 26:452-453. 1954.

3. Same as Method 5, Citation 1 through 9 of section 7.

APPENDIX A.5

KJELDAHL ANALYSIS METHOD

From: Methods for Chemical Analysis of Water and Wastes
EPA-600/4-79-020
March 1979

NITROGEN, KJELDAHL, TOTAL

Method 351.3 (Colorimetric; Titrimetric; Potentiometric)

STORET NO. 00625

1. Scope and Application
   1.1 This method covers the determination of total Kjeldahl nitrogen in drinking, surface and saline waters, domestic and industrial wastes. The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert the nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines.
   1.2 Three alternatives are listed for the determination of ammonia after distillation: the titrimetric method which is applicable to concentrations above 1 mg N/liter; the Nesslerization method which is applicable to concentrations below 1 mg N/liter; and the potentiometric method applicable to the range 0.05 to 1400 mg/1.
   1.3 This method is described for macro and micro glassware systems.
2. Definitions
   2.1 Total Kjeldahl nitrogen is defined as the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)_2SO_4$, under the conditions of digestion described below.
   2.2 Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free-ammonia value (Method 350.2, Nitrogen, Ammonia, this manual) from the total Kjeldahl nitrogen value. This may be determined directly by removal of ammonia before digestion.
3. Summary of Method
   3.1 The sample is heated in the presence of conc. sulfuric acid, K_2SO_4 and $HgSO_4$ and evaporated until SO_3 fumes are obtained and the solution becomes colorless or pale yellow. The residue is cooled, diluted, and is treated and made alkaline with a hydroxide-thiosulfate solution. The ammonia is distilled and determined after distillation by Nesslerization, titration or potentiometry.
4. Sample Handling and Preservation
   4.1 Samples may be preserved by addition of 2 ml of conc. H_2SO_4 per liter and stored at 4°C. Even when preserved in this manner, conversion of organic nitrogen to ammonia may occur. Preserved samples should be analyzed as soon as possible.
5. Interference
   5.1 High nitrate concentrations (10X or more than the TKN level) result in low TKN values. The reaction between nitrate and ammonia can be prevented by the use of an anion exchange resin (chloride form) to remove the nitrate prior to the TKN analysis.

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6. Apparatus

6.1 Digestion apparatus: A Kjeldahl digestion apparatus with 800 or 100 ml flasks and suction takeoff to remove SO_3 fumes and water.

6.2 Distillation apparatus: The macro Kjeldahl flask is connected to a condenser and an adaptor so that the distillate can be collected. Micro Kjeldahl steam distillation apparatus is commercially available.

6.3 Spectrophotometer for use at 400 to 425 nm with a light path of 1 cm or longer.

7. Reagents

7.1 Distilled water should be free of ammonia. Such water is best prepared by the passage of distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

NOTE 1: All solutions must be made with ammonia-free water.

7.2 Mercuric sulfate solution: Dissolve 8 g red mercuric oxide (HgO) in 50 ml of 1:4 sulfuric acid (10.0 ml conc. H_2SO_4 : 40 ml distilled water) and dilute to 100 ml with distilled water.

7.3 Sulfuric acid-mercuric sulfate-potassium sulfate solution: Dissolve 267 g K_2SO_4 in 1300 ml distilled water and 400 ml conc. H_2SO_4. Add 50 ml mercuric sulfate solution (7.2) and dilute to 2 liters with distilled water.

7.4 Sodium hydroxide-sodium thiosulfate solution: Dissolve 500 g NaOH and 25 g $Na_2S_2O_3 \cdot 5H_2O$ in distilled water and dilute to 1 liter.

7.5 Mixed indicator: Mix 2 volumes of 0.2% methyl red in 95% ethanol with 1 volume of 0.2% methylene blue in ethanol. Prepare fresh every 30 days.

7.6 Boric acid solution: Dissolve 20 g boric acid, H_3BO_3, in water and dilute to 1 liter with distilled water.

7.7 Sulfuric acid, standard solution: (0.02 N) 1 ml = 0.28 mg NH_3–N. Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of conc. H_2SO_4 (sp. gr. 1.84) to 1 liter with CO_2-free distilled water. Dilute 200 ml of this solution to 1 liter with CO_2-free distilled water. Standardize the approximately 0.02 N acid so prepared against 0.0200 N Na_2CO_3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3, oven-dried at 140°C, and diluting to 1 liter with CO_2-free distilled water.

NOTE 2: An alternate and perhaps preferable method is to standardize the approximately 0.1 N H_2SO_4 solution against a 0.100 N Na_2CO_3 solution. By proper dilution the 0.02 N acid can the be prepared.

7.8 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg NH_3–N. Dissolve 3.819 g NH_4Cl in water and make up to 1 liter in a volumetric flask with distilled water.

7.9 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg NH_3–N. Dilute 10.0 ml of the stock solution (7.8) with distilled water to 1 liter in a volumetric flask.

7.10 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g potassium iodide in a small volume of distilled water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 ml of distilled water. Dilute the mixture to 1 liter. The solution is stable for at least one year if stored in a pyrex bottle out of direct sunlight.

NOTE 3: Reagents 7.7, 7.8, 7.9, and 7.10 are identical to reagents 6.8, 6.2, 6.3, and 6.6 described under Nitrogen, Ammonia (Colorimetric; Titrimetric; Potentiometric-Distillation Procedure, Method 350.2).

8. Procedure

8.1 The distillation apparatus should be pre-steamed before use by distilling a 1:1 mixture of distilled water and sodium hydroxide-sodium thiosulfate solution (7.4) until the distillate is ammonia-free. This operation should be repeated each time the apparatus is out of service long enough to accumulate ammonia (usually 4 hours or more).

8.2 Macro Kjeldahl system

8.2.1 Place a measured sample or the residue from the distillation in the ammonia determination (for Organic Kjeldahl only) into an 800 ml Kjeldahl flask. The sample size can be determined from the following table:

Kjeldahl Nitrogen in Sample, mg/l	Sample Size ml
0–5	500
5–10	250
10–20	100
20–50	50.0
50–500	25.0

Dilute the sample, if required, to 500 ml with distilled water, and add 100 ml sulfuric acid-mercuric sulfate-potassium sulfate solution (7.3). Evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colorless or pale yellow. Continue heating for 30 additional minutes. Cool the residue and add 300 ml distilled water.

8.2.2 Make the digestate alkaline by careful addition of 100 ml of sodium hydroxide – thiosulfate solution (7.4) without mixing.

NOTE 5: Slow addition of the heavy caustic solution down the tilted neck of the digestion flask will cause heavier solution to underlay the aqueous sulfuric acid solution without loss of free-ammonia. Do not mix until the digestion flask has been connected to the distillation apparatus.

8.2.3 Connect the Kjeldahl flask to the condenser with the tip of condenser or an extension of the condenser tip below the level of the boric acid solution (7.6) in the receiving flask.

8.2.4 Distill 300 ml at the rate of 6–10 ml/min., into 50 ml of 2% boric acid (7.6) contained in a 500 ml Erlenmeyer flask.

8.2.5 Dilute the distillate to 500 ml in the flask. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks. For concentrations above 1 mg/l, the ammonia can be determined titrimetrically. For concentrations below this value, it is determined colorimetrically. The potentiometric method is applicable to the range 0.05 to 1400 mg/l.

8.3 Micro Kjeldahl system

8.3.1 Place 50.0 ml of sample or an aliquot diluted to 50 ml in a 100 ml Kjeldahl flask and add 10 ml sulfuric acid-mercuric sulfate-potassium sulfate solution (7.3). Evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colorless or pale yellow. Then digest for an additional 30 minutes. Cool the residue and add 30 ml distilled water.

8.3.2 Make the digestate alkaline by careful addition of 10 ml of sodium hydroxide-thiosulfate solution (7.4) without mixing. Do not mix until the digestion flask has been connected to the distillation apparatus.

8.3.3 Connect the Kjeldahl flask to the condenser with the tip of condenser or an extension of the condenser tip below the level of the boric acid solution (7.6) in the receiving flask or 50 ml short-form Nessler tube.

8.3.4 Steam distill 30 ml at the rate of 6–10 ml/min., into 5 ml of 2% boric acid (7.6).

8.3.5 Dilute the distillate to 50 ml. For concentrations above 1 mg/l the ammonia can be determined titrimetrically. For concentrations below this value, it is determined colorimetrically. The potentiometric method is applicable to the range 0.05 to 1400 mg/l.

8.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically, or potentiometrically, as described below.

8.4.1 Titrimetric determination: Add 3 drops of the mixed indicator (7.5) to the distillate and titrate the ammonia with the 0.02 N H_2SO_4 (7.7), matching the endpoint against a blank containing the same volume of distilled water and H_3BO_3 (7.6) solution.

8.4.2 Colorimetric determination: Prepare a series of Nessler tube standards as follows:

ml of Standard 1.0 ml = 0.01 mg NH_3–N	mg NH_3–N/50.0 ml
0.0	0.0
0.5	0.005
1.0	0.010
2.0	0.020
4.0	0.040
5.0	0.050
8.0	0.080
10.0	0.10

Dilute each tube to 50 ml with ammonia free water, add 1 ml of Nessler Reagent (7.10) and mix. After 20 minutes read the absorbance at 425 nm against the blank. From the values obtained for the standards plot absorbance vs. mg NH_3-N for the standard curve. Develop color in the 50 ml diluted distillate in exactly the same manner and read mg NH_3-N from the standard curve.

8.4.3 Potentiometric determination: Consult the method entitled Nitrogen, Ammonia: Potentiometric, Ion Selective Electrode Method, (Method 350.3) in this manual.

8.4.4 It is not imperative that all standards be treated in the same manner as the samples. It is recommended that at least 2 standards (a high and low) be digested, distilled,

and compared to similar values on the curve to insure that the digestion-distillation technique is reliable. If treated standards do not agree with untreated standards the operator should find the cause of the apparent error before proceeding.

9. Calculation

9.1 If the titrimetric procedure is used, calculate Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{(A - B)N \times F \times 1{,}000}{S}$$

where:
A = milliliters of standard 0.020 N H_2SO_4 solution used in titrating sample.
B = milliliters of standard 0.020 N H_2SO_4 solution used in titrating blank.
N = normality of sulfuric acid solution.
F = milliequivalent weight of nitrogen (14 mg).
S = milliliters of sample digested.

If the sulfuric acid is exactly 0.02 N the formula is shortened to:

$$\text{TKN, mg/l} = \frac{(A - B) \times 280}{S}$$

9.2 If the Nessler procedure is used, calculate the Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{A \times 1{,}000}{D} \times \frac{B}{C}$$

where:
A = mg NH_3–N read from curve.
B = ml total distillate collected including the H_3BO_3.
C = ml distillate taken for Nesslerization.
D = ml of original sample taken.

9.3 Calculate Organic Kjeldahl Nitrogen in mg/l, as follows:
Organic Kjeldahl Nitrogen = TKN –(NH_3–N.)

9.4 Potentiometric determination: Calculate Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{B}{D} \times A$$

where:
A = mg NH_3–N/l from electrode method standard curve.
B = volume of diluted distillate in ml.
D = ml of original sample taken.

10. Precision

10.1 Thirty-one analysts in twenty laboratories analyzed natural water samples containing exact increments of organic nitrogen, with the following results:

Increment as Nitrogen, Kjeldahl mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as Bias, %	Accuracy as Bias, mg N/liter
0.20	0.197	+15.54	+0.03
0.31	0.247	+ 5.45	+0.02
4.10	1.056	+ 1.03	+0.04
4.61	1.191	- 1.67	-0.08

(FWPCA Method Study 2, Nutrient Analyses)

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 437, Method 421 (1975).
2. Schlueter, Albert, "Nitrate Interference In Total Kjeldahl Nitrogen Determinations and Its Removal by Anion Exchange Resins", EPA Report 600/7-77-017.

APPENDIX B

AMMONIA ANALYSIS PROCEDURES

From: methods for Chemical Analysis of Water and Wastes
EPA-600/4-79-020
March 1979

NITROGEN, AMMONIA

Method 350.2 (Colorimetric; Titrimetric; Potentiometric – Distillation Procedure)

STORET NO. Total 00610
Dissolved 00608

1. Scope and Application
   1.1 This distillation method covers the determination of ammonia-nitrogen exclusive of total Kjeldahl nitrogen, in drinking, surface and saline waters, domestic and industrial wastes. It is the method of choice where economics and sample load do not warrant the use of automated equipment.
   1.2 The method covers the range from about 0.05 to 1.0 mg NH_3–N/l for the colorimetric procedure, from 1.0 to 25 mg/l for the titrimetric procedure, and from 0.05 to 1400 mg/l for the electrode method.
   1.3 This method is described for macro glassware; however, micro distillation equipment may also be used.
2. Summary of Method
   2.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. The ammonia in the distillate can be determined colorimetrically by nesslerization, titrimetrically with standard sulfuric acid with the use of a mixed indicator, or potentiometrically by the ammonia electrode. The choice between the first two procedures depends on the concentration of the ammonia.
3. Sample Handling and Preservation
   3.1 Samples may be preserved with 2 ml of conc. H_2SO_4 per liter and stored at 4°C.
4. Interferences
   4.1 A number of aromatic and aliphatic amines, as well as other compounds, both organic and inorganic, will cause turbidity upon the addition of Nessler reagent, so direct nesslerization (i.e., without distillation), has been discarded as an official method.
   4.2 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out. Volatile alkaline compounds, such as certain ketones, aldehydes, and alcohols, may cause an off-color upon nesslerization in the distillation method. Some of these, such as formaldehyde, may be eliminated by boiling off at a low pH (approximately 2 to 3) prior to distillation and nesslerization.
   4.3 Residual chlorine must also be removed by pretreatment of the sample with sodium thiosulfate before distillation.

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5. Apparatus

5.1 An all-glass distilling apparatus with an 800–1000 ml flask.

5.2 Spectrophotometer or filter photometer for use at 425 nm and providing a light path of 1 cm or more.

5.3 Nessler tubes: Matched Nessler tubes (APHA Standard) about 300 mm long, 17 mm inside diameter, and marked at 225 mm ±1.5 mm inside measurement from bottom.

5.4 Erlenmeyer flasks: The distillate is collected in 500 ml glass-stoppered flasks. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks.

6. Reagents

6.1 Distilled water should be free of ammonia. Such water is best prepared by passage through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

NOTE 1: All solutions must be made with ammonia-free water.

6.2 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg NH_3–N. Dissolve 3.819 g NH_4Cl in distilled water and bring to volume in a 1 liter volumetric flask.

6.3 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg. Dilute 10.0 ml of stock solution (6.2) to 1 liter in a volumetric flask.

6.4 Boric acid solution (20 g/l): Dissolve 20 g H_3BO_3 in distilled water and dilute to 1 liter.

6.5 Mixed indicator: Mix 2 volumes of 0.2% methyl red in 95% ethyl alcohol with 1 volume of 0.2% methylene blue in 95% ethyl alcohol. This solution should be prepared fresh every 30 days.

NOTE 2: Specially denatured ethyl alcohol conforming to Formula 3A or 30 of the U.S. Bureau of Internal Revenue may be substituted for 95% ethanol.

6.6 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g of potassium iodide in a small amount of water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 ml of water. Dilute the mixture to 1 liter. If this reagent is stored in a Pyrex bottle out of direct sunlight, it will remain stable for a period of up to 1 year.

NOTE 3: This reagent should give the characteristic color with ammonia within 10 minutes after addition, and should not produce a precipitate with small amounts of ammonia (0.04 mg in a 50 ml volume).

6.7 Borate buffer: Add 88 ml of 0.1 N NaOH solution to 500 ml of 0.025 M sodium tetraborate solution (5.0 g anhydrous $Na_2B_4O_7$ or 9.5 g $Na_2B_4O_7 \cdot 10H_2O$ per liter) and dilute to 1 liter.

6.8 Sulfuric acid, standard solution: (0.02 N, 1 ml = 0.28 mg NH_3–N). Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of conc. H_2SO_4 (sp. gr. 1.84) to 1 liter with CO_2-free distilled water. Dilute 200 ml of this solution to 1 liter with CO_2-free distilled water.

NOTE 4: An alternate and perhaps preferable method is to standardize the approximately 0.1 N H_2SO_4 solution against a 0.100 N Na_2CO_3 solution. By proper dilution the 0.02 N acid can then be prepared.

6.8.1 Standardize the approximately 0.02 N acid against 0.0200 N Na_2CO_3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3, oven-dried at 140°C, and diluting to 1000 ml with CO_2-free distilled water.

6.9 Sodium hydroxide, 1 N: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 liter.

6.10 Dechlorinating reagents: A number of dechlorinating reagents may be used to remove residual chlorine prior to distillation. These include:

a. Sodium thiosulfate (1/70 N): Dissolve 3.5 g $Na_2S_2O_3 \cdot 5H_2O$ in distilled water and dilute to 1 liter. One ml of this solution will remove 1 mg/l of residual chlorine in 500 ml of sample.

b. Sodium arsenite (1/70 N): Dissolve 1.0 g $NaAsO_2$ in distilled water and dilute to 1 liter.

7. Procedure

7.1 Preparation of equipment: Add 500 ml of distilled water to an 800 ml Kjeldahl flask. The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.

7.2 Sample preparation: Remove the residual chlorine in the sample by adding dechlorinating agent equivalent to the chlorine residual. To 400 ml of sample add 1 N NaOH (6.9), until the pH is 9.5, checking the pH during addition with a pH meter or by use of a short range pH paper.

7.3 Distillation: Transfer the sample, the pH of which has been adjusted to 9.5, to an 800 ml Kjeldahl flask and add 25 ml of the borate buffer (6.7). Distill 300 ml at the rate of 6–10 ml/min. into 50 ml of 2% boric acid (6.4) contained in a 500 ml Erlenmeyer flask.

NOTE 5: The condenser tip or an extension of the condenser tip must extend below the level of the boric acid solution.

Dilute the distillate to 500 ml with distilled water and nesslerize an aliquot to obtain an approximate value of the ammonia-nitrogen concentration. For concentrations above 1 mg/l the ammonia should be determined titrimetrically. For concentrations below this value it is determined colorimetrically. The electrode method may also be used.

7.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically or potentiometrically as described below.

7.4.1 Titrimetric determination: Add 3 drops of the mixed indicator to the distillate and titrate the ammonia with the 0.02 N H_2SO_4, matching the end point against a blank containing the same volume of distilled water and H_3BO_3 solution.

7.4.2 Colorimetric determination: Prepare a series of Nessler tube standards as follows:

ml of Standard 1.0 ml = 0.01 mg NH_3–N	mg NH_3–N/50.0 ml
0.0	0.0
0.5	0.005
1.0	0.01
2.0	0.02
3.0	0.03
4.0	0.04
5.0	0.05
8.0	0.08
10.0	0.10

Dilute each tube to 50 ml with distilled water, add 2.0 ml of Nessler reagent (6.6) and mix. After 20 minutes read the absorbance at 425 nm against the blank. From the values obtained plot absorbance vs. mg NH_3–N for the standard curve. Determine the ammonia in the distillate by nesslerizing 50 ml or an aliquot diluted to 50 ml and reading the absorbance at 425 nm as described above for the standards. Ammonia-nitrogen content is read from the standard curve.

7.4.3 Potentiometric determination: Consult the method entitled Nitrogen, Ammonia: Selective Ion Electrode Method (Method 350.3) in this manual.

7.5 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree with undistilled standards the operator should find the cause of the apparent error before proceeding.

8. Calculations

8.1 Titrimetric

$$\text{mg/l } NH_3 - N = \frac{A \times 0.28 \times 1{,}000}{S}$$

where:

A = ml 0.02 N H_2SO_4 used.

S = ml sample.

8.2 Spectrophotometric

$$\text{mg/l } NH_3 - N = \frac{A \times 1{,}000}{D} \times \frac{B}{C}$$

where:

A = mg NH_3–N read from standard curve.

B = ml total distillate collected, including boric acid and dilution.

C = ml distillate taken for nesslerization.

D = ml of original sample taken.

8.3 Potentiometric

$$mg/l\ NH_3 - N = \frac{500}{D} \times A$$

where:

A = mg NH_3–N/1 from electrode method standard curve.

D = ml of original sample taken.

9. Precision and Accuracy

9.1 Twenty-four analysts in sixteen laboratories analyzed natural water samples containing exact increments of an ammonium salt, with the following results:

Increment as Nitrogen, Ammonia mg N/liter	Precision as Standard Deviation mgN/liter	Accuracy as Bias, %	Accuracy as Bias, mg N/liter
0.21	0.122	–5.54	–0.01
0.26	0.070	–18.12	–0.05
1.71	0.244	+0.46	+0.01
1.92	0.279	–2.01	–0.04

(FWPCA Method Study 2, Nutrient Analyses)

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 410, Method 418A and 418B (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D1426–74, Method A, p 237 (1976).

PART III

SPECIFIC ION ELECTRODE METHOD

Ammonia

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SPECIFIC ION ELECTRODE

INTRODUCTION

Aqueous ammonia concentrations may be determined using a specific ion electrode attached to a standard pH meter. This procedure may be used to measure dissolved ammonia or ammonium ion in aqueous solutions. After proper pH adjustment, the ammonia electrode responds logarithmically to the level of ammonia in the solution. The response of the electrode to ammonia concentration is recorded in millivolt readings directly from the pH meter. A standard calibration curve is prepared by ploting the log of the ammonia concentration vs. the millivolt response. The samples are then analyzed accordingly and their concentration are calculated from the calibration curve. The method is simple and quick, requiring little sample preparation.

THEORY

The electrode consists of an internal reference solution separated from the sample solution by a hydrophobic gas-permeable membrane. The principle of operation involves the passage of dissolved ammonia in the solution through the membrane until the partial pressures of ammonia on both sides of the membrane are equal. As the ammonia passes through the membrane, it dessolves in the filling solution and to a small extent reacts reversibly with the water in the filling solution:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The relationship between ammonia, ammonium and hydroxide ion is given by the following equation:

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = \text{constant}\cdot(K)$$

Since the internal filling solution contains ammonium chloride at a sufficiently high level so that the ammonium ion concentration is fixed, then this relationship may be rewritten:

$$[OH^-] = [NH_3] \cdot \text{constant}$$

This shows the relationship between the free ammonia in the sample and the hydroxide ion concentration in the filling solution. As the NH_3 migrates through the membrane, the concentration of hydroxide ion changes in the internal reference solution, thus changing the potential of the electrode sensing element in a Nerstean manner:

$$E = E_0 - S \log [OH^-]$$

Therefore,

$$E = E_1 - S \log [NH_3]$$

From the above two equations, one can see that the sensing element changes with the change in concentration of NH_3 in the sample. In order to convert ammonium ion to ammonia, the pH of the sample must be adjusted with standard base to a pH of 11 or greater according to the following equation:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

APPRATUS

Ammonia Electrode, Model 95-10, Orion Research Incorporated
Model 701 Digital pH Meter
Electrode Holder, Cat. No. 92-00-01, Orion Research Incorporated
Magnetic Stirrer with stirring bar

REAGENTS

Sodium Hydroxide, 5 Normal, NaOH

Prepare by dissolving 200 grams of reagent grade sodium hydroxide in a 1-liter volumetric flask and dilute to mark with ammonia-free distilled-deionized water. This will give you a 0.1 Molar solution.

INTERFERENCES

Ionic species cannot cross the gas-permeable membrane, so they cannot affect electrode operation. The level of ions in solution can, however, change the solubility of ammonia to some degree, affecting the electrode calibration. Best results are obtained if standards and samples have about the same level of ions (and other dissolved species) present. Therefore, the samples analyzed must be diluted to a dissolved species concentration of 0.2 Molar or less.

The only other interference recorded is water vapor, which can diffuse across the membrane. The addition of NaOH will help equalize the osmotic pressure on both sides of the membrane so that the water vapor will not diffuse across the membrane.

STANDARD CURVE

Prepare a standard calibration curve by making serial dilutions from the 10^{-1} M ammonium sulfate solution to prepare 10^{-2} M, 10^{-3} M, 10^{-4} M, 10^{-5} M, and 10^{-6} M standards. Starting with the least concentrated standard, 10^{-6} M, and working to the most concentrated standard, 10^{-2} M, take a 10-ml aliquot of each, add 0.2 ml of 5-N NaOH and place the electrode in the standard solution until a constant millivolt reading is obtained. Use a stirring bar to agitate the sample. Repeat this procedure until all standards have been analyzed. Between each standard, rinse the electrode with several portions of distilled-deionized water. Once all standards have been analyzed, a calibration curve as in

Specific Ion Electrode

Calibration Graph

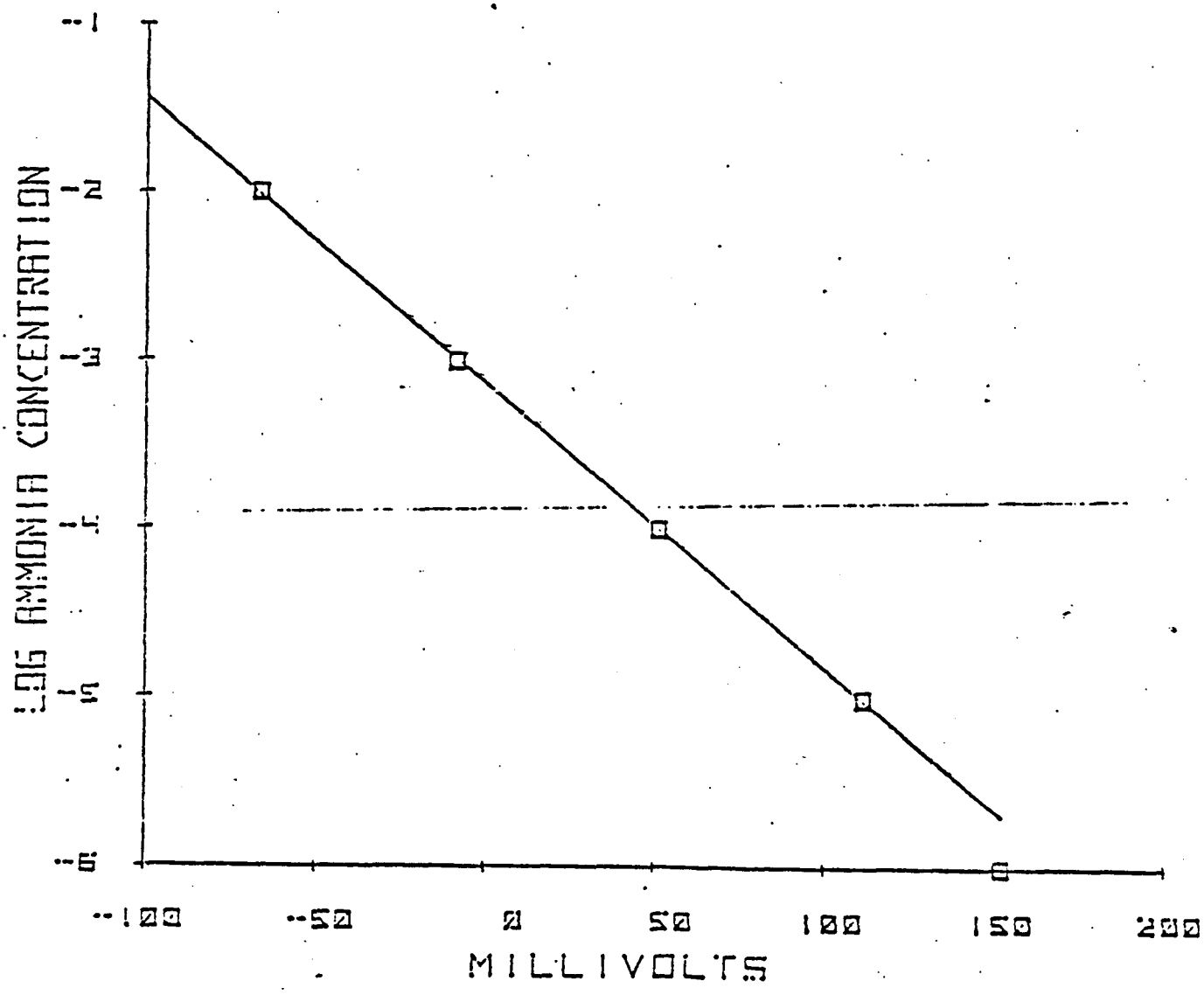


Figure 6

CONC.	TRIALS	MEAN	SIGMA
1E-06	2	152.4	0.00
1E-05	2	111.9	0.14
1E-04	2	51.7	0.28
1E-03	2	-8.1	0.00
1E-02	2	-66.3	0.14

CORRECTION FACTOR= 1.04820E-06
SLOPE= -0.016822610
INTERCEPT = -3.124855002

Figure 6 should be produced. Between 10^{-5} M and 10^{-2} M the curve is linear, but a correction factor must be added to produce a linear curve between 10^{-6} M and 10^{-5} M ammonia concentration.

SAMPLE ANALYSIS

Because the probe wash, probe plug and impinger catches are very acidic, it is necessary to dilute them so the total concentration of dissolved species is ~0.2 M. To reach this level, 1 ml aliquots are diluted by a factor of 20 with distilled-deionized water then treated as normal samples. Record the mv reading after a constant value is observed. For best results, start with the least concentrated samples (probe plug and probe wash), then analyze the impinger catches. Also, the samples and standards should be at the same temperature and should be agitated by the stirring bar at the same rate.

From the standard curve, record the millivolt readings from the samples and note concentrations.

CALCULATIONS

$$\text{mg } NH_3 = (\text{moles}/1000 \text{ ml}) \ (D_1) \ (D_2) \ (17 \text{ grams/mole}) \ (1000 \text{ mg/g})$$

$$\text{ug}/M^3 = (\text{mg } NH_3) \ (10^3 \text{ ug/mg})/M^3$$

$$\text{ppm} = (\text{ug}/M^3) \ \left(\frac{0.02445}{17}\right)$$

where: D_1 = dilution volume of original sample, ml

D_2 = dilution factor of sample analyzed

M^3 = volume of flue gas sampled corrected to standard conditions, M^3

APPENDIX C

SAMPLE PRESERVATION ANALYSIS DATA

Includes:

C.1 Field Sample Preservation
C.2 Laboratory Sample Preservation

APPENDIX C.1

FIELD SAMPLE PRESERVATION

m = $HgCl_2$
A = H_2SO_4

AGRICO RTD

SCRUBBER STACK GAS SAMPLE PRESERVATION

NA = not analyzed
S = sample coil not used
A $\frac{43 \times 2}{25} = 3.4$
B $\frac{32 \times 2}{25} = 2.6$

* DISTILLED ON THIS DATE. SUBSEQUENT ANALYSIS ON 11 JAN 79
** " . SUBSEQUENT ANALYSIS OF $NH_3 \cdot D$ and WW on 12 JAN 79

		V_T		F_D		X_1	C	$\frac{(X_1 - C)}{35} \times F_D \times \frac{V_T}{1000} \times 1.765$ (WW only)		F_D		X_1	C			F_D		X_1	C	
	Sample no.	Sample volume (ml)		Dilution Factors	Abs.	mg NH_3/sample	Blank corr mg NH_3/sample	MASS (mg)			Abs.			MASS (mg)			Abs.			MASS (mg)
m	1 NH_3	975			NA						NA					25×10	.244	86	0	419
	$NH_3 \cdot D$		12/26	10×25	.392	104	NC	507		10×25	.293	90	3.4 A	422		10×1×25	.268	83	3.3	389
	WW		12/26	10×5	.240	18.5	7	92.7		10×5	.154	54	12.8	70.9		10×1×5	.218	67.5	13	93.8
	2	990			NA						NA					25×10	.178	62	0	307
			"	10×25	.237	63	NC	312		10×25	.182	58	3.4	270		10×1×25	.213	66.5	3.3	313
			"	10×5	.154	51.5	7	77.7		10×5	.176	61	12.8	84.5		10×1×5	.194	60	13	82.1
	3	1100			NA						NA					25×10	.186	65	0	358
			"	10×25	.234	62	NC	341		10×25	.210	67	3.4	350		10×1×25	.210	65.5	3.3	342
			"	10	.202	54	35	DIGEST SOL not added		10×1	.410	131.5	64	26.2		10×1×1	.420	129.5	65	25.0
	4	970			NA						NA					25×10	.180	63.5	0	308
			"	10×25	.256	68	NC	330		10×25	.222	70.5	3.4	325		10×1×25	.230	72	3.3	333
			"	10	.630	167.5	35	45.4		10×1	.500	159	64	32.5		10×1×1	.412	127	65	21.2
	5	1095			NA						NA					25×10	.154	55	0	301
			"	10×25	.212	56	NC	307		10×25	.198	63	3.4	326		10×1×25	.185	58	3.3	299
			"	10	.405	108	35	28.3		10×1	.270	85.5	64	9.9		10×1×1	.320	100	65	13.5
	6	1005			NA						NA					25×10	.153	54	0	271
			12/27	10×25	.206	55	NC	276		10×25	.190	60.5	3.5	286		10×1×25	.165	51	3.3	240
			"	10	.599	161	35	44.3		10×1	.478	142.5	64	27.8		10×1×1	.254	78	65	4.6
A	1 NH_3	975			NA						NA					25×10	.291	102	0	497
	$NH_3 \cdot D$		12/26	10×25	.351	93	NC	453		10×25	5	—	3.4	—		10×1×25	.315	98	3.3	462
	WW A		12/26	10×5	.186	49	7	72.2		10×50	.378	113	1.3	1922		10×1×5	.188	58	13	77.4
	2	950			NA						NA					25×10	.188	66	0	327
			"	10×25	.266	71	NC	351		10×25	5	—	3.4	—		10×1×25	.228	71	3.3	335
			"	10×5	.155	51.5	7	77.7		10×25	.272	90.5	2.6	268		10×1×5	.244	76	13	110
	3	1160			NA						NA					25×10	.175	61.5	0	338
			"	10×25	.252	67	NC	369		10×25	.210	67	3.4	350		10×1×25	.230	72	3.3	378
			"	10	.385	102	35	26.1		10×1	.350	114	64	19.4		10×1×1	.265	82	65	6.6
	4	970			NA						NA					25×10	.206	72	0	345
			"	10×25	.279	74	NC	359		10×25	.275	72	3.4	333		10×1×25	.275	86	3.3	401
			"	10	.678	180.5	35	49.8		10×1	.600	190	64	43.1		10	.520	160	65	32.5
	5	1055			NA						NA					25×10	.164	58	0	318
			"	10×25	.382	102	NC	558 cloudy		10×25	.222	70.5	3.4	367		10×1×25	.182	57	3.3	294
			"	10	cloudy	—	35	—		10×1	.235	79	64	5.8		10	.390	120	65	21.3
	6	1005	12/27		NA						NA					25×10	.158	56	0	281
			"	10×25	.223	59	NC	296		10×25	.192	61	3.4	289		10×1×25	.185	58	3.3	275
				10	.490	130.5	35	37.9		10×1	.305	100	64	12.8		10	.168	52	65	—

Agnew R&D

M = H_2SO_4
A = H_2SO_4
NA = not analyzed

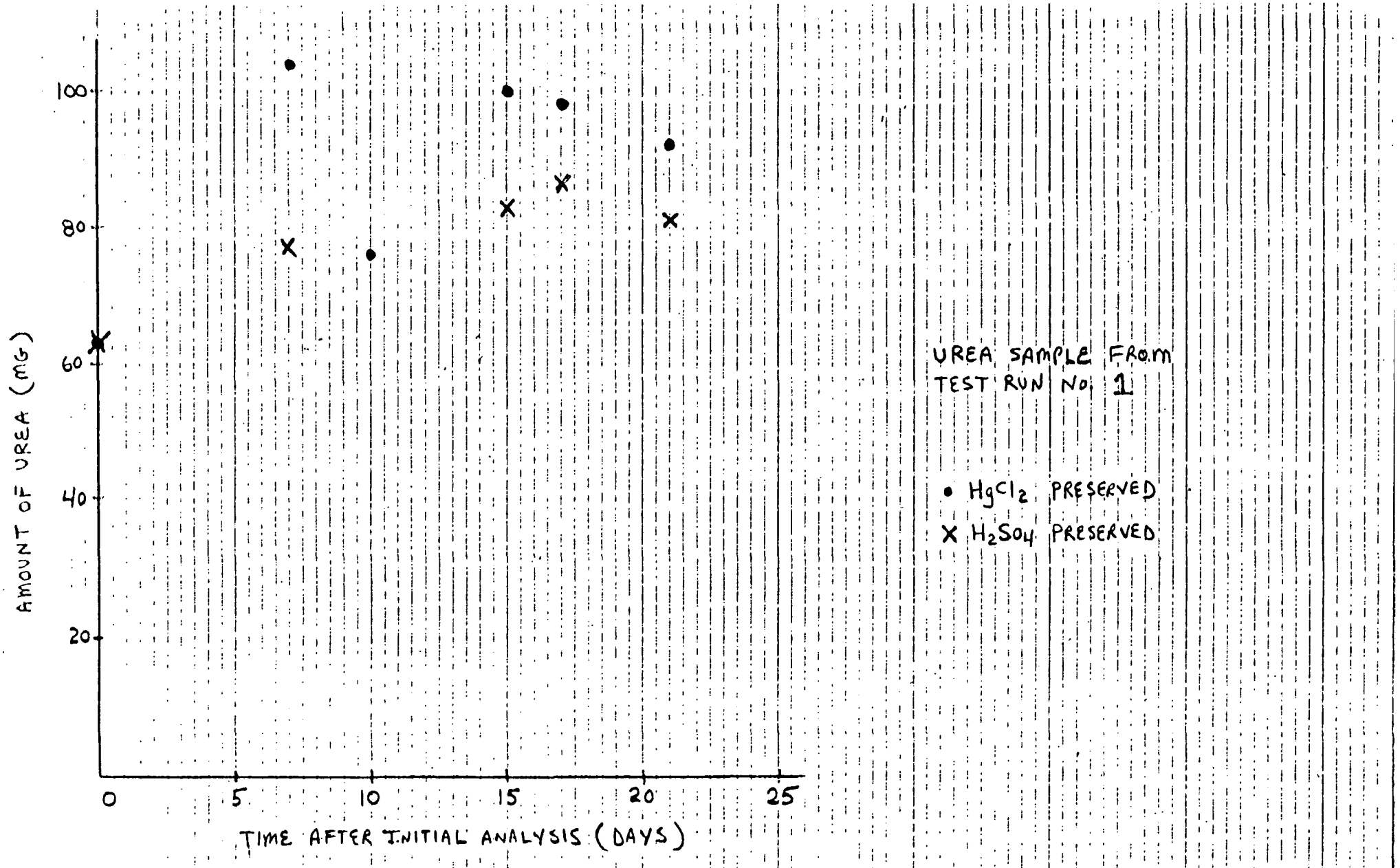
Agnew Scrubber Stack Gas Sample Preservation

* Distilled on this date. Subsequent NH_3-D and urea analyses done on 6, 15 and 16 January 1979.

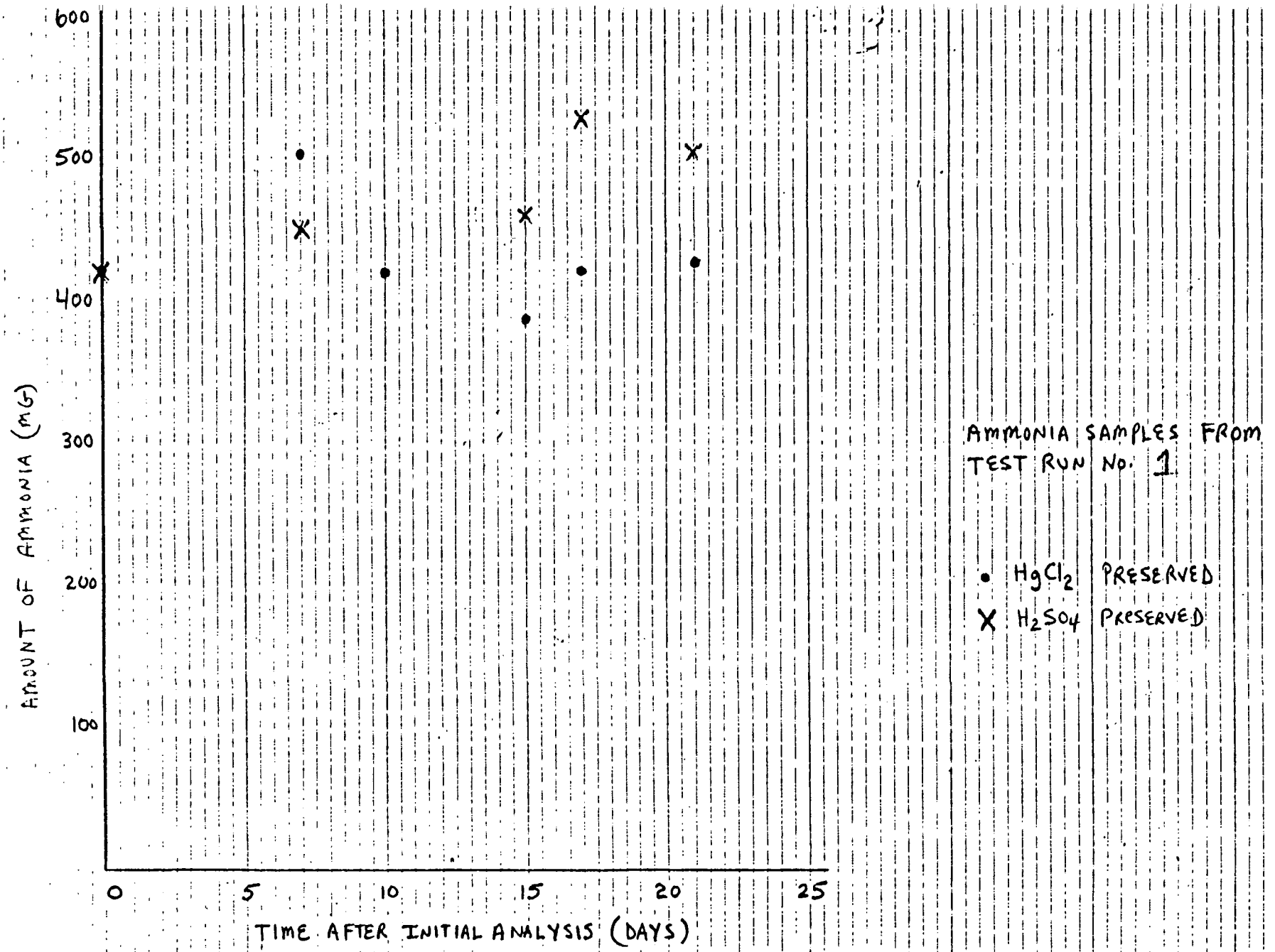
B $30 = \frac{71.5}{5}$ C average of 1/4/79, 1/5 and 1/9.
A $2.5 = \frac{62}{25}$ D $\frac{4}{5} = 3$ E $\frac{50}{5} = 10$

** Distilled on this date. Analyses performed on 6, 17 and 18 January 1979

		5 Jan 79 *							9 Jan 79 **				
	Sample No.	V Sample volume (ml)	F_D Dilution Factors	Abs.	X_1 µg NH_3/50 ml	C Blank Corr. µg NH_3/50 ml	$\frac{(X_1-C)}{50} \times F_D \times \frac{V}{1000}$ mass (mg)	mg/Nm³	F_D	Abs.	X_1	C	mass (mg)
M	1 NH_3 NH_3-D urea	975	25x10	.284	98	0	478		25x10	.275	91	0	444
			10x1x25	.260	79.5	2.5 A	424		10x1x25	.267	91	3 D	429
			10x1x5	.190	66	13	91.2		10x1x5	.213	60	10 E	56.0
	2	950	25x10	.211	73	0	361		25x10	.200	67	0	332
			10x1x25	.191	66.5	3 B	295		10x1x25	.120	38	3	173
			10x1x5	.193	57.5	12 C	79.5		10x1x5	.210	59	10	85.6
	3	1100	25x10	.252	86.5	0	476		25x10	.260	67	0	369
			10x1x25	.154	58	3	303		10x1x25	.131	42	3	215
			10x1x1	.500	148	61 C	33.8		10x1x1	.439	122.5	52	27.4
	4	970	25x10	.241	83	0	403		25x10	.220	73	0	354
			10x1x25	.191	66.5	2.5	310		10x1x25	.141	45.5	3	206
			10x1x1	.372	122.5	65	19.7		10x1x1	.605	169	52	40.1
	5	1055	25x10	.175	61	0	334		25x10	.180	60	0	329
			10x1x25	.169	53.5	3	276		10x1x25	.121	39	3	198
			10x1x1	.539	159.5	61 C	38.1		10x1x1	.337	94.5	52	16.4
	6	1005	25x10	.169	59	0	296		25x10	.170	56.5	0	284
			10x1x25	.167	53	3	251		10x1x25	.122	39.5	3	183
			10x1x1	.560	166	61 C	37.3		10x1x1	.578	161	52	38.7
A	1 NH_3 NH_3-D urea	975	25x10	.292	100	0	488		25x10	.290	96.5	0	470
			10x1x25	.334	111	2.5	529		10x1x25	.339	107	3	507
			10x1x5	.172	60.5	13	81.7		10x1x5	.151	54	10	75.7
	2	950	25x10	.297	101	0	500		25x10	.220	73	0	361
			10x1x25	.212	66.5	3	314		10x1x25	.222	70	3	332
			10x1x5	.189	56	12 C	76.9		10x1x5	.183	52	10	73.4
	3	1100	25x10	.225	78	0	429		25x10	.203	68	0	374
			10x1x25	.211	66.5	3	349		10x1x25	.219	69	3	363
			10x1x1	.538	159	61 C	38.1		10x1x1	.414	118.5	52	25.8
	4	970	25x10	.238	82	0	398		25x10	.260	86.5	0	420
			10x1x25	.243	84	2.5	395		10x1x25	.232	73.5	3	342
			10x1x1	.410	133	65	121.3		10x1x1	.556	166	52	35.0
	5	1095	25x10	.155	68	0	372		25x10	.200	67	0	367
			10x1x25	.190	60	3	312		10x1x25	.158	63	3	329
			10x1x1	.339	100	61 C	15.1		10x1x1	.323	91	52	15.1
	6	1005	25x10	.180	63	0	317		25x10	.186	62	0	312
			10x1x25	NA	—	3	—		10x1x25	.208	66	3	317
				NA	—	—	—		10x1x1	.500	139.5	52	31.0



GRANULATOR C SCRUBBER OUTLET GASEOUS SAMPLE PRESERVATION



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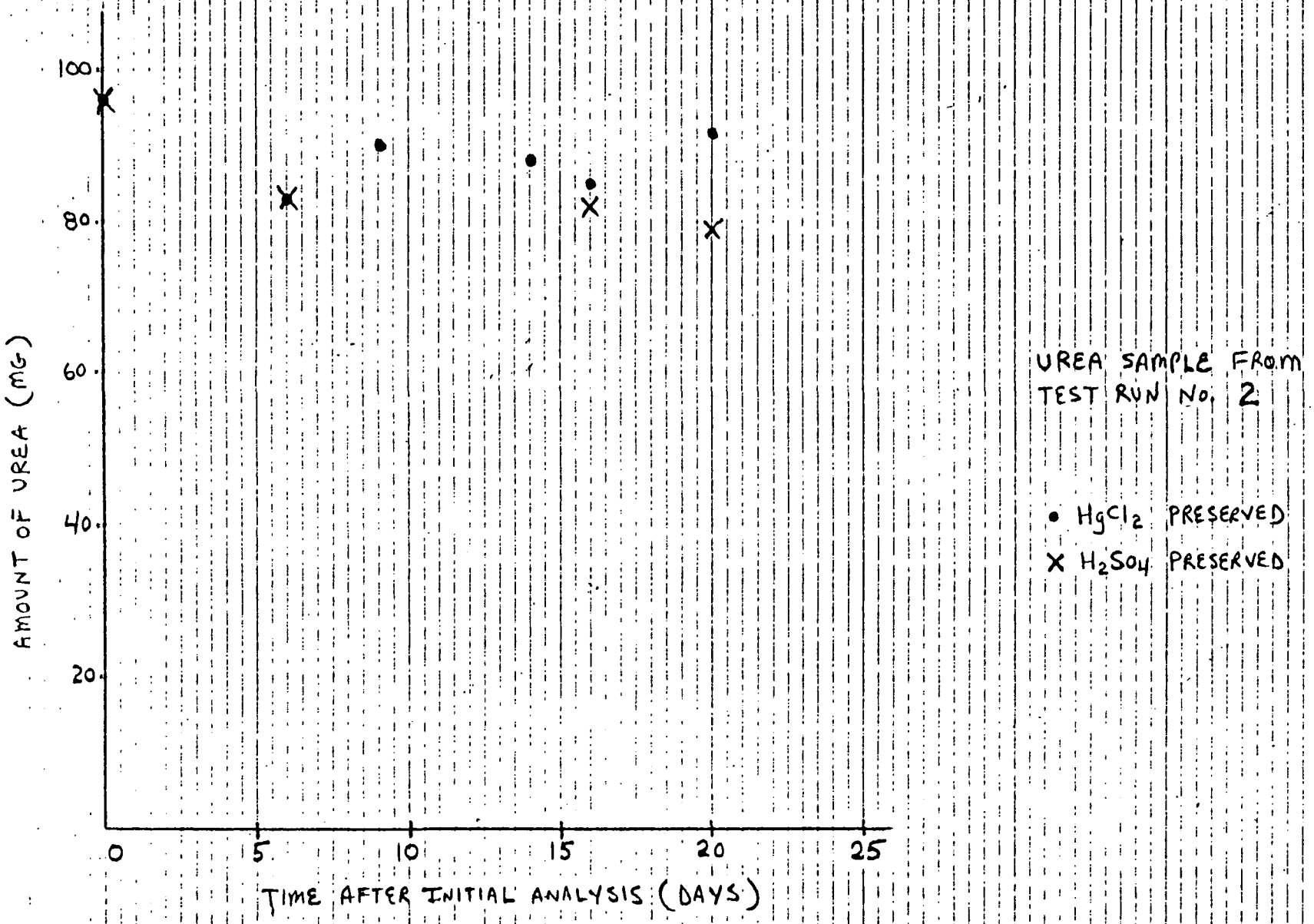

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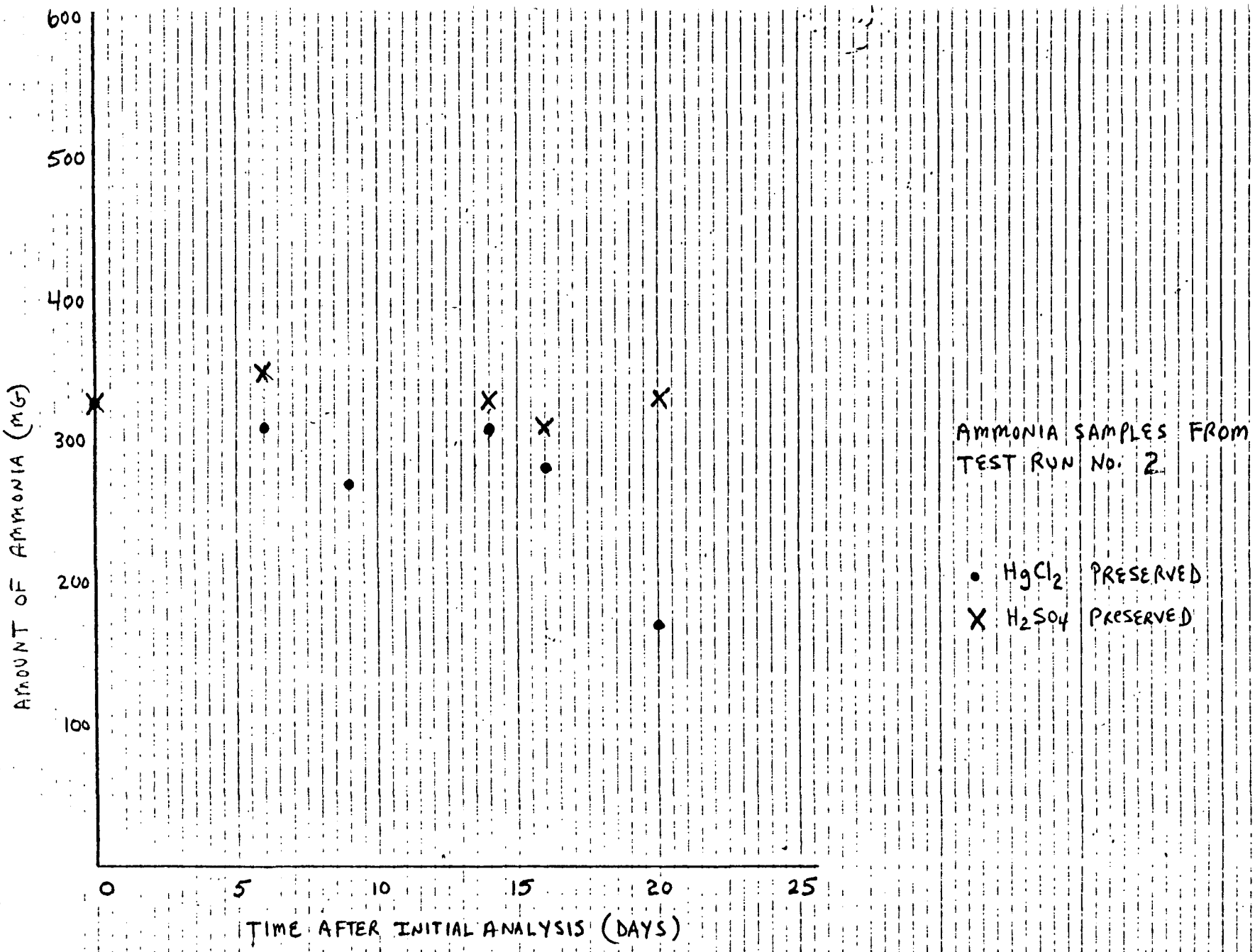

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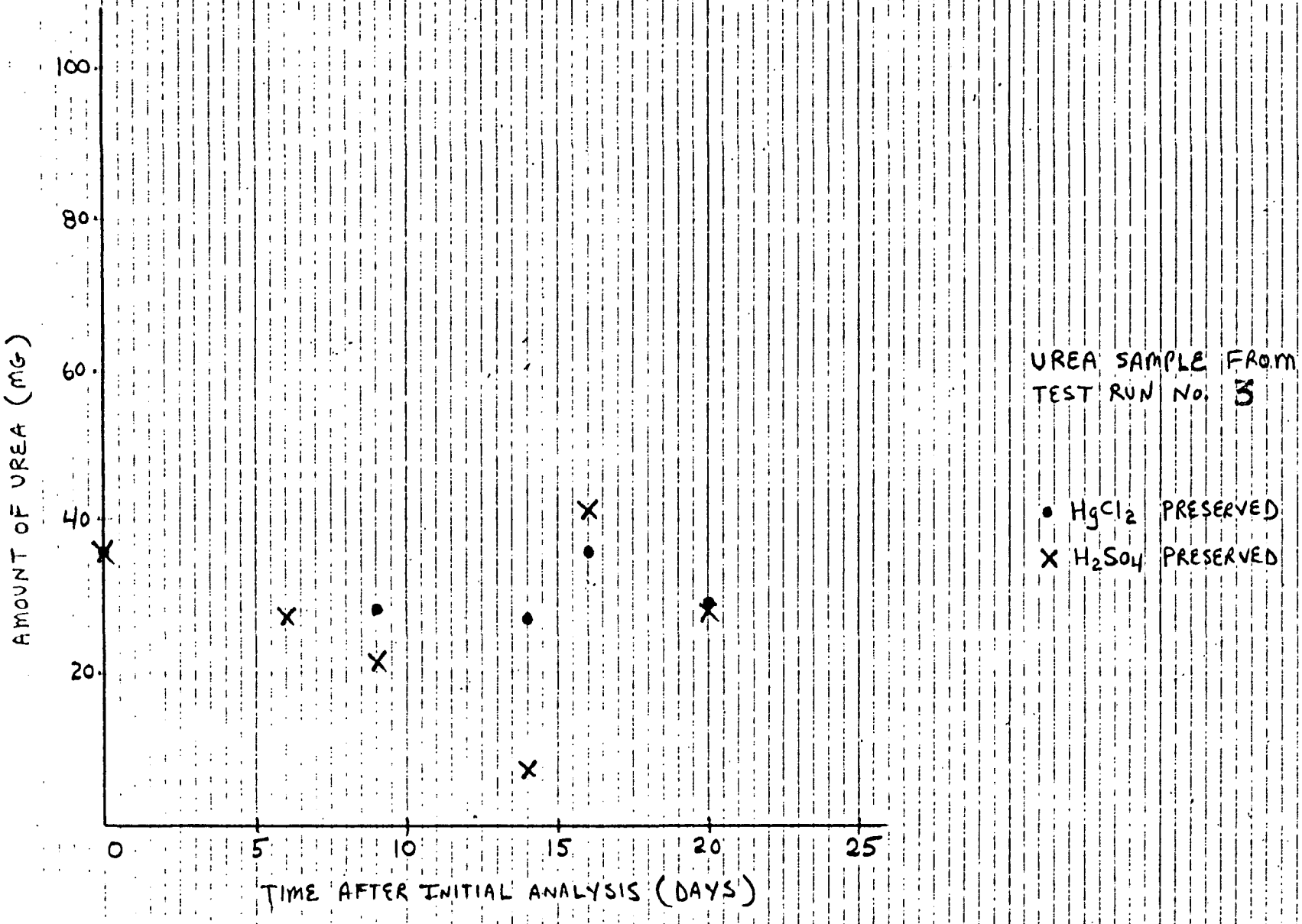

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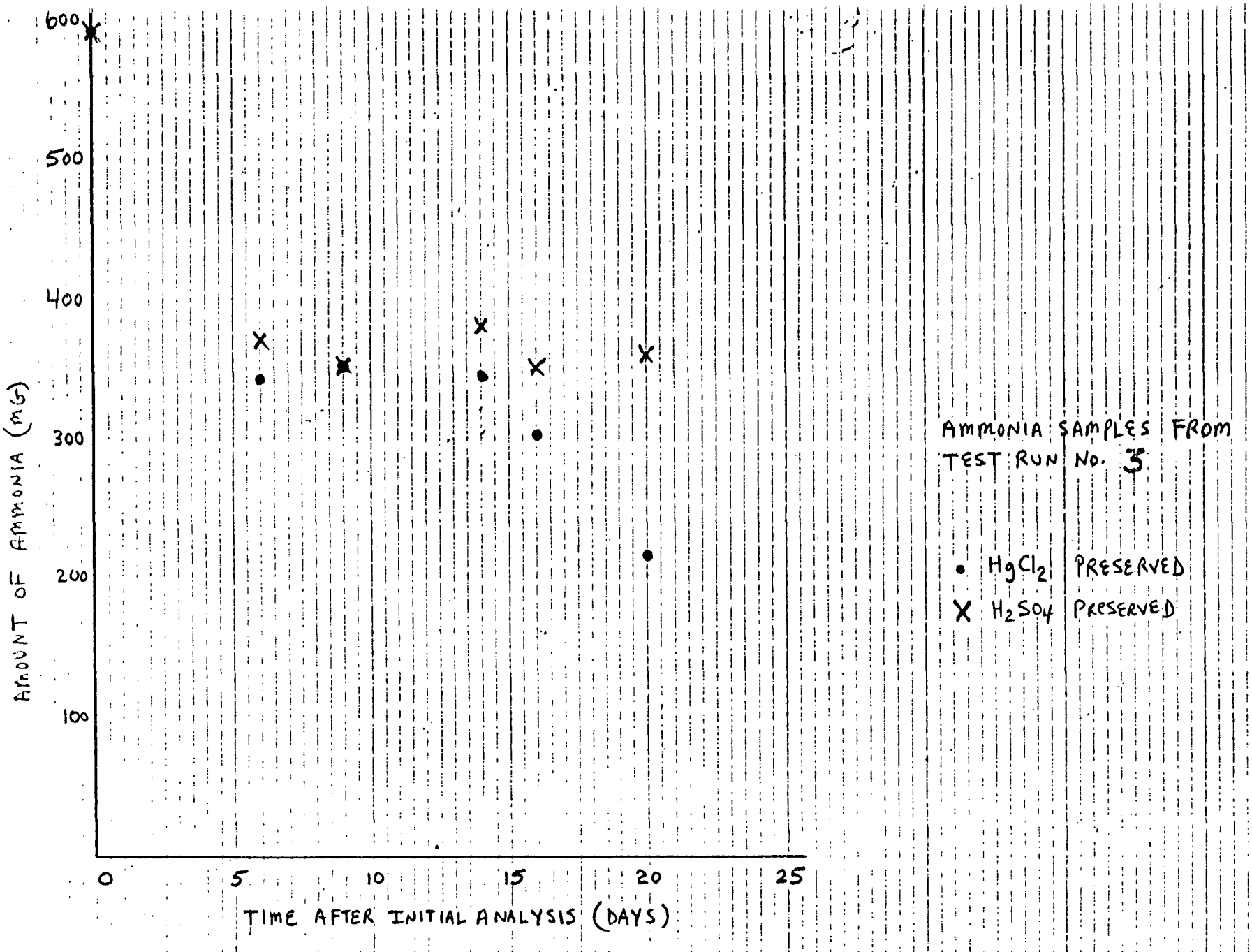

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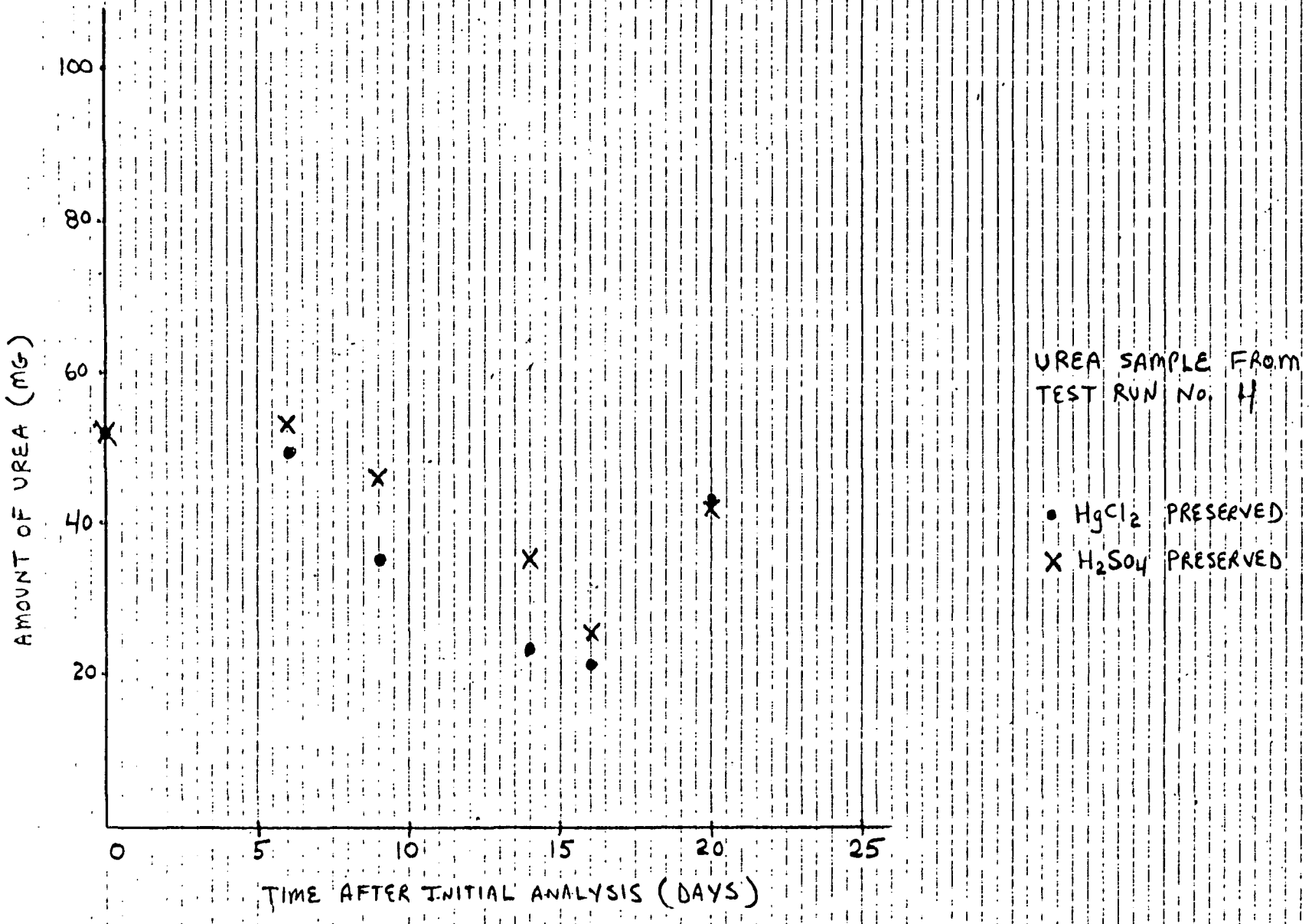

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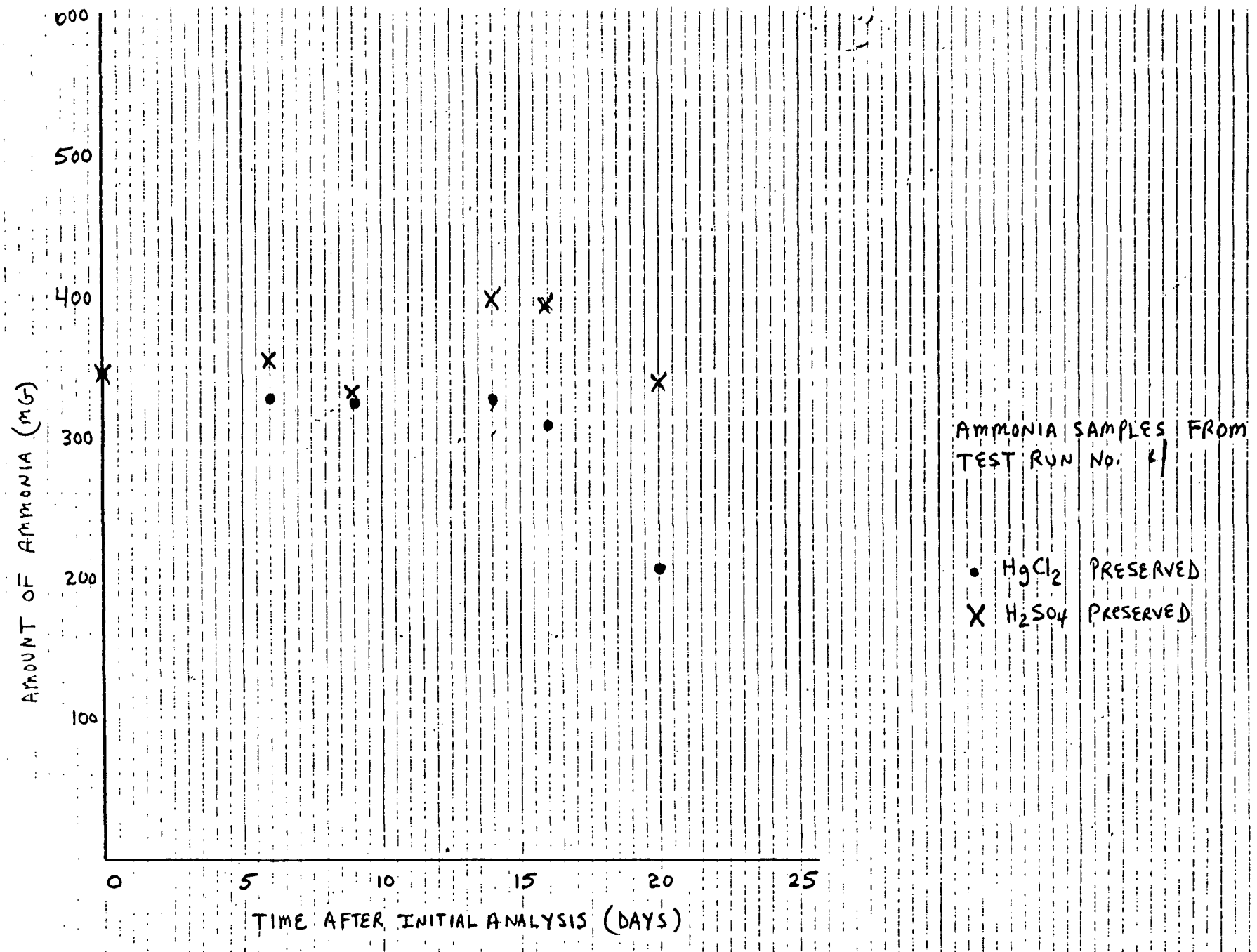

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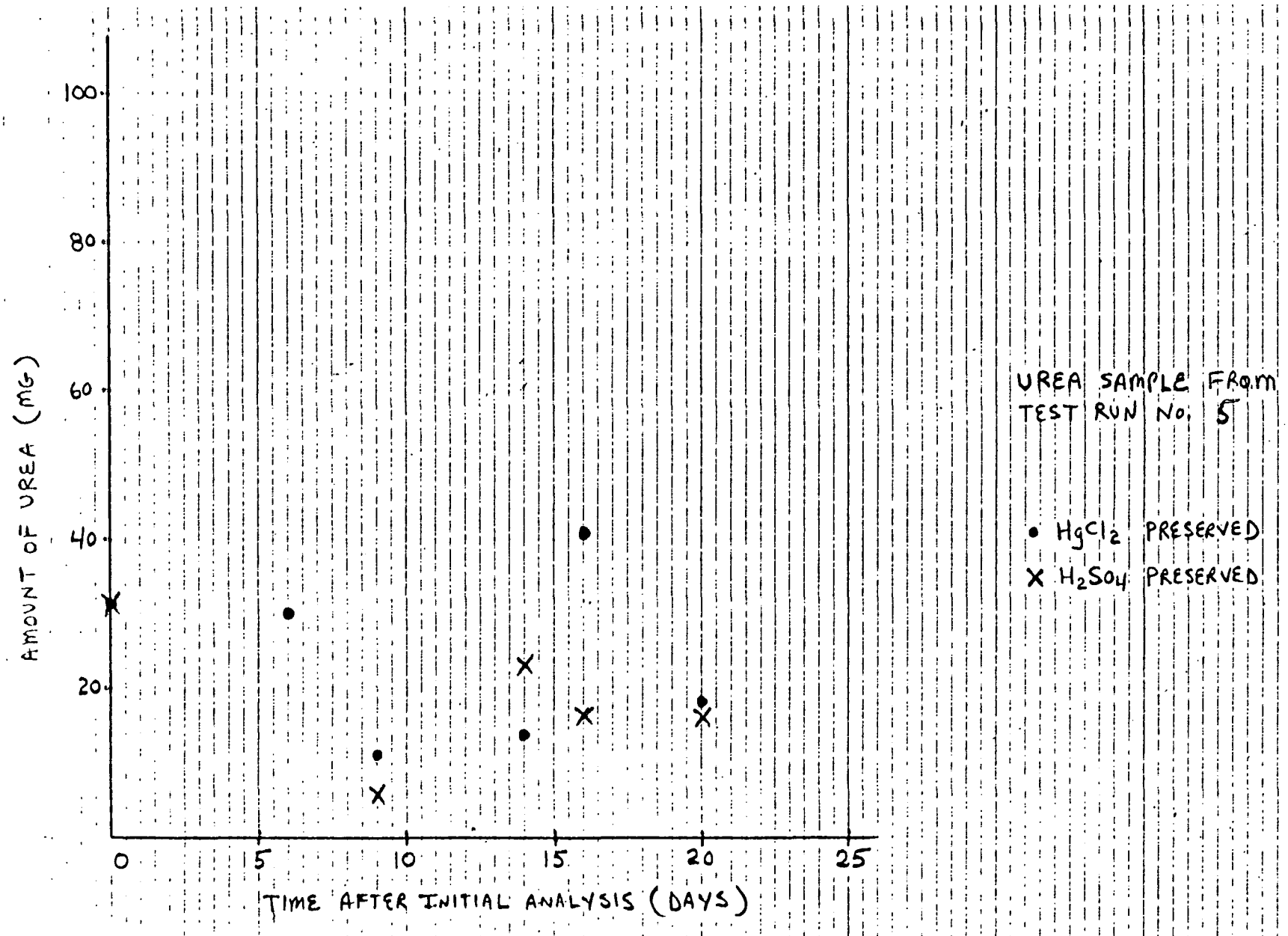

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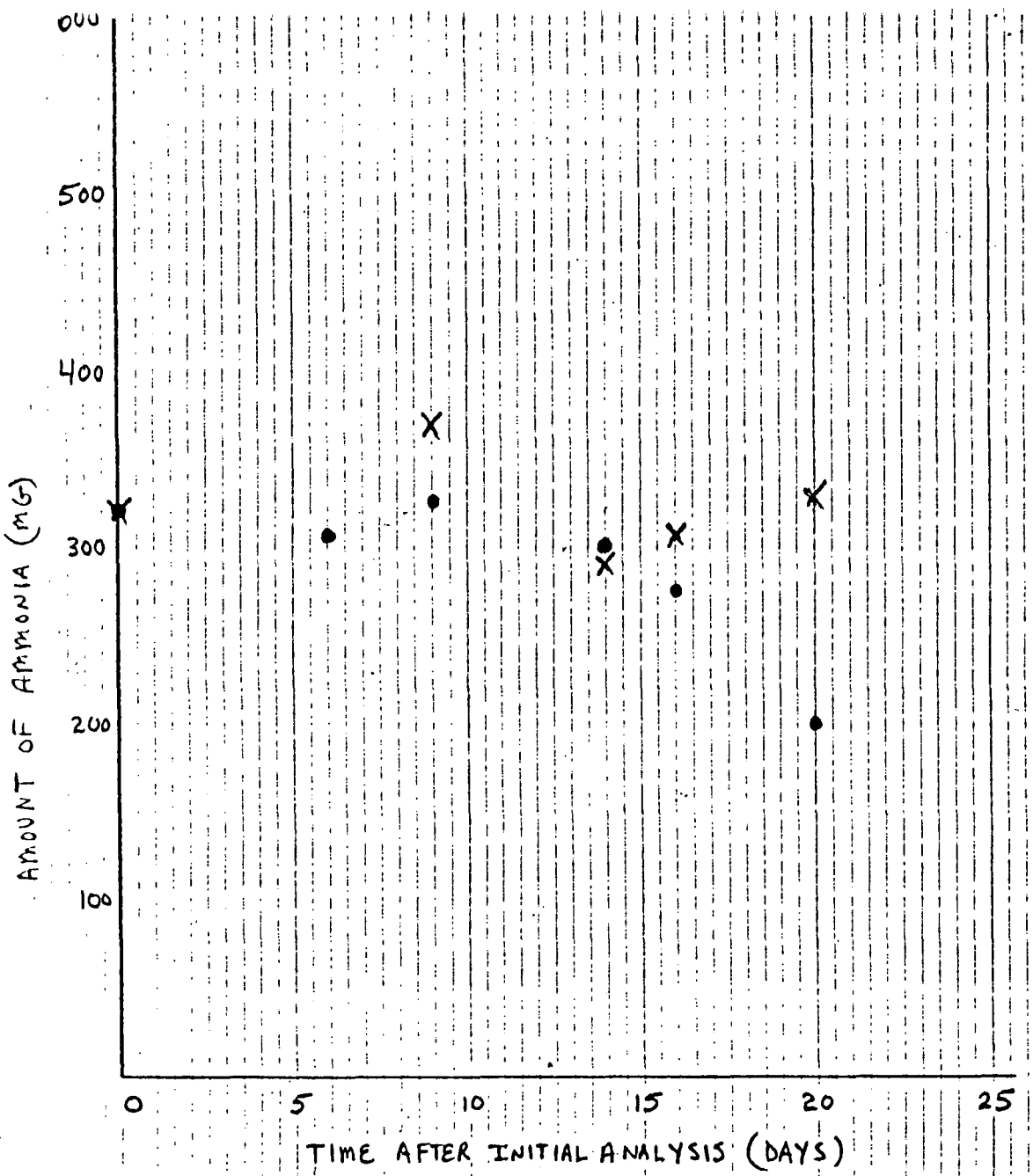

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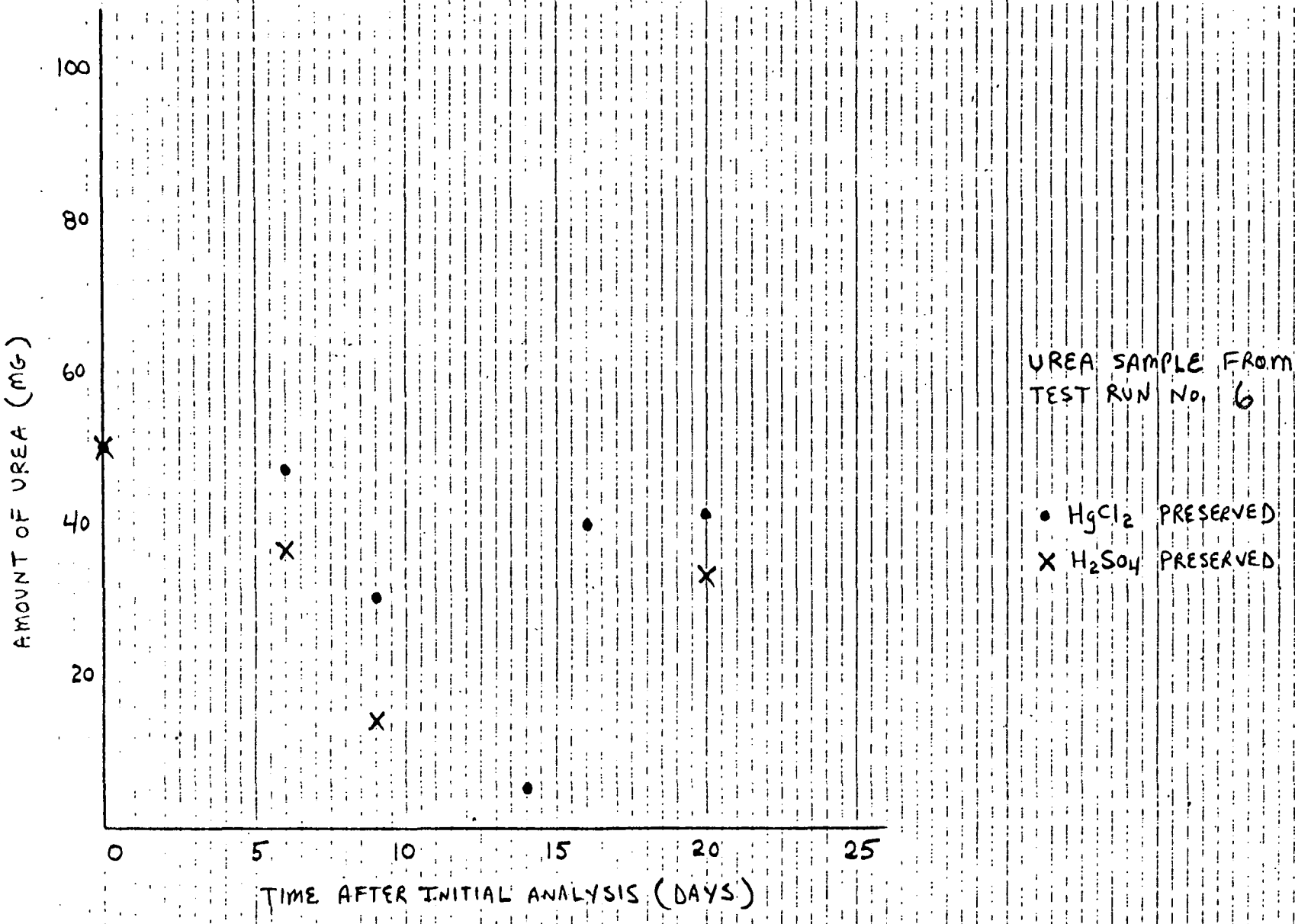

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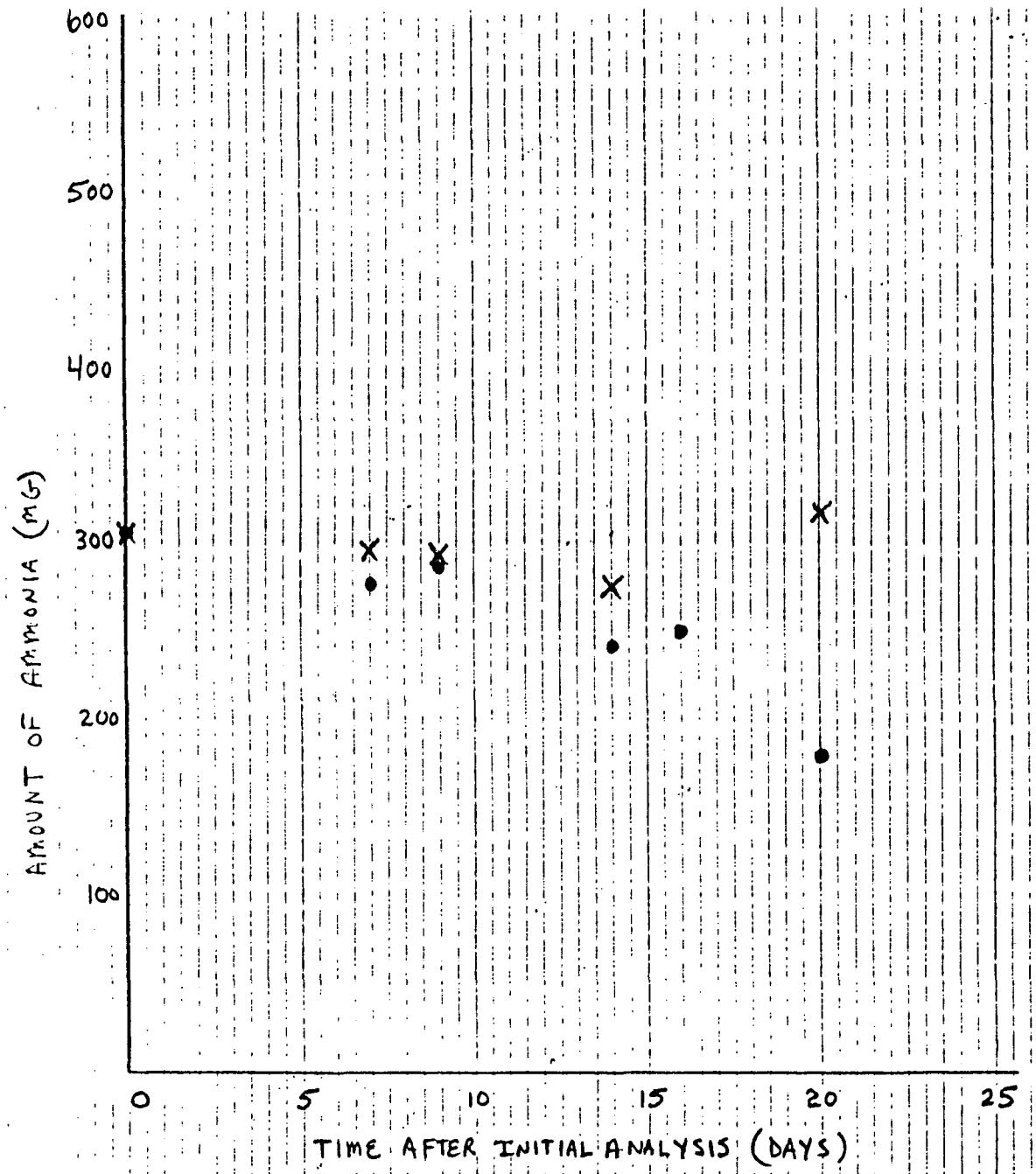

GRANULATOR C SCRUBBER OUTLET GASEOUS SAMPLE PRESERVATION

TITLE AGRICO - RESET

from Page No. ____

12/26/78
8 da

Sample	Original Distillate	Vol NH_3 distilled	Vol Urea Distillate	
Stock 1 $HgCl_2$ 1 H_2SO_4	25.0	250 ml	250 ml	9 -
Stock 2 $HgCl_2$ 2 H_2SO_4				7 da
Stock 3 $HgCl_2$ 3 H_2SO_4				
Stock 4 $HgCl_2$ 4 H_2SO_4				
Stock 5 $HgCl_2$ H_2SO_4				
~~Stock 6 $HgCl_2$~~				

Alone distilled NH_3 on Tues 12/26, then added digestion solution to residue 9 da

12/27/78

Stock 6 $HgCl_2$ 6 H_2SO_4	25.0 ml	250 ml	250 ml	

To Page No. ____

Witnessed & Understood by me,	Date	Invented by	Date
		Recorded by	

Project No. 82938-01
Book No. 82988-1 TITLE AGRICO - RESET

Page No. ___ Calculation pp 22-23 12/27/78

Sample	µg analyzed	~~mg Reconstitute~~ aliquot distilled	~~mg Reconstitute~~ Volume distillate	mg Reconstitute	2nd dilution factor	Original Sample Vol	total mg	µg/mg
via air								
L-Outlet 1	105.5	~~1.0~~	~~500~~	5.0	5→500			2110.
ch 2	84			5.0	5→100	990 mg	~~333~~	
ch 3	84					1100	370	
ch 4	93.5					970	363	
ch 5	74.0					1095	342	
ch 6	75.0					1005	302	
nk 2	~~54.0~~							
L-Inlet 4	59.0			1.0	5→500			5,900
L-Outlet 4	120.0			5.0	5→500			2,400
nk 1	~~5 µg~~							nd
Filed NH3								
L-Outlet 1	146.5	10.0	500	0.5	~~nonsolution~~			14650
ch 2	66.5	50.0	500	6.0	—	recalcu	329	
3	~~54~~ 98.5				—		~~542~~	593 gm
4	72				—		349	
5	59.0				—		323	
6	61.0				—		306	
nk 2	5.0			50.0	—			0.1 µg/ml
L-Inlet 4	121	10.0		1.0	—			6050
L-Out 4	228/100	10.0		1.0/½	—			~~11,400~~ 10,000
Ia nk 1	5 µg	500	500	50.0	—			0.1 µg/ml
a							mg/liter	
L-Outlet 1	52.0	10.0	~~500~~ 500	1.0	5→500			459,000
ch 2	135	50.0	500	25.0	—	recalcu		← 70.0
3	49.5				—			← 33.6
4	76.5				—			← ~~54.4~~ 43.1
5	43.0				—			← ~~33.2~~ 29.1
6	72.5				—			← 47.0
nk 2	12.5	500		50.0	—			0.35 µg/ml
L-Inlet 4	163.5	10.0		10.0	5→100			24,858
L-Outlet 4	96.0	10.0		5.0	2→500			423,600
L-Inlet 1	166.5	10.0		10.0	5→100			33,397
nk 1	5 µg	500						

To Page No.

Checked & Understood by me ___ Date ___ Invented by ___ Date ___

TITLE AGRICO - RESET

Project No. 32958-01
Book No. 82988-1

From Page No. [illegible]

New Investigation Set I pp 24+25 10/27/78

Note. Volume of NH_3 + Low Distillate 250 ml
2nd + Outlet 5.0 ml aliquot distilled
Stack Samples 25.0 ml aliquot distilled

Standard	
20 µg NH_3	.074
40	.139
100	.391
150	.599
200	.729

Samples from pp 24+25

Samples - NH_3	Distilled 2nd Outlet	Aliquot/Some Muller	Abs.	equivalent µg NH_3	µg/ml NH_3 *
Set 2 In	5->100	5 ml	.128	34	6,800 ✓ ✓ dk
2 Out		0.5	.400	105	10,650 ✓ ✓ JMM 2-1
3 In	5->100	5 ml	.132	35.0	7,000 ✓
3 Out		0.5	.332	88.0	8800
5 In	5->100	5 ml	.124	33.0	6600
5 Out		0.5	.346	92.0	9200 ✓
6 In	5->100	5 ml	.117	31.0	6200 ✓
6 Out		0.5	.313	83.5	8,350 ✓
TRC Blank		50.0	.316 (cloudy, but not yellow)		
" " Repeat		50.0	.323 " " " "		

Stack		original Value				total mg NH_3
1	$HgCl_2$	975	2 ml	.392	104	507 ✓
1	H_2SO_4	~~99~~		.351	93	453 ✓
2	$HgCl_2$	990		.237	63	312 ✓ dk JMM 2-12
2	H_2SO_4			.266	71	351
3	$HgCl_2$	1100		.234	62	341 ✓
3	H_2SO_4			.252	67	368.5 ✓
4	$HgCl_2$	970		.256	68	330 ✓
4	H_2SO_4			.279	74	359 ✓
5	$HgCl_2$	1095		.212	56	307
5	H_2SO_4			~~.375~~ .382	Cloudy	Cloudy
6	$HgCl_2$	1005		.206	55	276 ✓
6	H_2SO_4			.223	59	296 ✓

*Samples were not corrected for Blank since the aliquot of sample taken was at least 1/25th the Blank and the blank reading was falsely high due to cloudy nesses - It appeared close to blank visually.

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Witnessed & Understood by me,	Date	Invented by	Date
[illegible]		Recorded by	

Project No. 82988-01
Book No. 82988-1 TITLE AGRICO - RESET

m Page No. 37

Set I pp 24-25

multiply by urea factor 1.765

Sample Urea

	2 mod Dilution	mg/Kjeldahl Tube	Abs	µg NH3	mg/ml NH3 Urea
Set 2 2 in	2 -> 50	5.0	.330	188.0	38.830 ✓
2 Out	1 -> 50	1.0	.370	98.5	434.6 ✓
3 2 in	2 -> 50	5.0	.330	88.0	38.83 ✓
3 out	1 -> 50	1.0	.426	113.0	498.6 ✓
5 2 in	2 -> 50	5.0	.299	79.5	35.08 ✓
5 Out	1 -> 50	1.0	.411	109.5	483.2 ✓
6 2 in	2 -> 50	5.0	.307	~~5 X 2~~ 81.5	~~37.06~~ 35.96 ✓
6 Out	1 -> 50	1.0	.387	103	454.5 ✓
TRC Blank	—	50.0	.132 - sample is 36 µg yellow-clear		.72 µg/ml NH3 for ml of diluted

		Sample Volume	mg					total mg Urea	Blank
Stack 1	$HgCl_2$	975 ml	~~50.0 ml~~	10.0 ml	.240 ✓	63.5	-7.2	109.3 ✓	96.4
	H_2SO_4			10.0	.186 ✓	49.0	-7.2	84.3	71.0
2	$HgCl_2$	990		10.0	.194	51.5	-7.2	90.0 ✓	77.4
	H_2SO_4			10.0	.195	51.5	-7.2 ✓	90.0	77.4
3	$HgCl_2$	* digestion sol'n 1100 ml not added - low	50.0	.202		54.0	-36	—	
	H_2SO_4		50.0	.385		103.0	-36	39.6	27.2
4	$HgCl_2$	970	50.0	.630		167.5	-36 ✓	57.4	41.0
	H_2SO_4		50.0	.678		180.5	-36	61.8	47.5
5	$HgCl_2$	1095	50.0	.405		108.0	-36	41.7	28.8
	H_2SO_4		50.0	1.15	light yellow cloudy				
6	$HgCl_2$	1005	50.0	.599 ✓		160.1	-36	56.8	44.0
	H_2SO_4		50.0	.490 ✓		130.5	-36	46.3	35.5

Blank

To Page No.

tnessed & Understood by me,	Date	Invented by	Date
		Recorded by	

TITLE AGRICO - RESET

Project No. 5000-1
Book No. 88783-1

From Page No.

Reset I

12/27/78

NH_3 as is

		2nd Dilution	Aliquot/combined
Stack 1	Hg	2 → 5000	5.0 mls
1	H_2SO_4		
2	Hg		
2	H_2SO_4		
3	Hg		
3	H_2SO_4		
4	Hg		
4	H_2SO_4		
5	Hg		
5	H_2SO_4		
6	Hg		
6	H_2SO_4	✓	✓

Above not done - lack of time

To Page No.

Witnessed & Understood by me,	Date	Invented by	Date
		Recorded by	

Project No. 82988-01
Book No. 82988-1 TITLE AGRICO - RESET
Set 2

From Page No. — Sample Pup Set II Urea + NH_3 distilled to 250 mL 12/25/78

aliquot 5.0 mL

Inlet 1 $HgCl_2$ H_2SO_4 Urea may be low transfer Urea

Outlet 1 $HgCl_2$ H_2SO_4

Inlet 4 $HgCl_2$ H_2SO_4

Outlet 4 $HgCl_2$ H_2SO_4

In 2 $HgCl_2$ H_2SO_4

Out 2 $HgCl_2$ H_2SO_4 5.0 mL

Inlet 3 $HgCl_2$ H_2SO_4

Out 3 $HgCl_2$ H_2SO_4

In 5 $HgCl_2$ H_2SO_4

Out 5 $HgCl_2$ H_2SO_4

12/27/78

In 6 $HgCl_2$ H_2SO_4 5.0

Out 6 $HgCl_2$ H_2SO_4

Blank 2

analyzed p 32-33

M = Mercuric Chloride Preservation
A = H_2SO_4 Preservation

To Page No.

Witnessed & Understood by me, | Date | Invented by | Date

TITLE AGRICO - RESET

Project No. [illegible]
Book No. [illegible]-1

From Page No.

Direct Nesslerization ammonia 1/5/79

Stock 1000 µg/ml NH_3 Dilute 10.0 ml → 500 ⇒ 20 µg/ml NH_3

Standards total µg NH_3	ml/50 ml flask	Abs
0	0	.000
20	1.	.050
40	2.	.106
100	5.	.243
160	8.	.503
200	10.	.649

Sample			Final Dilution	Aliquot		Equivalent µg NH_3	total mg NH_3	ppm NH_3
St 1	M	475 ml	2 → 50.0	5.0	.234	95	475	
	A				.242	100.	488	
St 2	M	990 ml			.211	73	361	dc JMM
	A				.297	101	500	
St 3	M	1100 ml			.252	86.5	476	
	A				.225	78.0	429	dc JMM
St 4	M	970 ml			.241	83.0	402	402.6
	A				.238	82.0	398	
St 5	M	1095 ml			.175	61.0	334	
	A				.195	68.0	372	
St 6	M	1095 ml			.169	59.0	296	296.5
	A				.180	63.0	316	316.6
								µg/m NH_3
Inlet 1	M		5 → 500	2.0	.362	119		5950
	A			2.0	.395	129		6450
Outlet 1	M			10.0	.308	104		1040
	A		5 → 500	5.0	.426	137	dc JMM	2740
Inlet 4	M		5 → 500	2.0	.306	103		5150
	A			2.0	.432	139		6950
Outlet 4	M			10.0	.307	103.5		1035
	A			2.0	.323	77.0	dc JMM	3950

Calculation p38

To Page No.

Witnessed & Understood by me,	Date	Invented by	Date
[illegible] 1/24/79		Recorded by	

Project No. 82988-01
Book No. 82988-1 TITLE AGRICO - RESET

Nesslerization of Some Urea and Distilled NH_3 from Set 4 pp 39-40 1/6/78

								Blank corrected see p57
	Dilution	2nd Dilution	Ml. Neutralized	Abs.	µg equivalent NH_3		ppm NH_3 mg/ml	
1 m	5 mL→250		1.0	.325	109		5450 ✓	5378
1 A			1.0	.384	125.5		6275 ✓	6203
1 m		5→25	2.0	.153	54		6750 ✓	6678
1 A		5→25	2.0	.176	61.5		7625 ✓	7553
4 m			1.0	.281	96.5		4825 ✓	4753
A			1.0	.288	99		4950 ✓	4878
4 m		5→25	2.0	.160	56		7000 ✓	6928
A		5→25	2.0	.173	60.5		~~7625~~ 7563	7491
	Distillation						total mg NH_3	
1 m	25→250	—	2.0	.260	89.5	975 ml	4363	4322
A		—		.334	111.0		541	527
4 m		—		.191	66.5	970 ml	322	308
A		—		.243	84.0		409	343
								Blank corrected
	Distillation						µg/ml Urea	
1 m	5→250	2→50	5.0	.250	86.0	× urea factor	~~759~~ 37,978	
A		2→50	5.0	.242	83.0	×1.765	~~732~~ 36,624	
1 m		1→50	1.0	.352	116.5		~~10,281~~ 514,056	
A		1→50	1.0	.380	124.5		549,356 ✓	
4 m		2→50	5.0	.235	82		36,182 ✓	
A		2→50	5.0	.230	79.5		35,079 ✓	
4 m		1→50	1.0	.353	116.5		514,056 ✓	
A		1→50	1.0	.369	121.0		533,912.5 ✓	
							total mg Urea	
m	25→250	—	10.0	.190	66.0	970 ml	113.8 *	
A		—	10.0	.172	60.5		104.1 ✓ *	
m		—	50.0	.372	122.5	970 ml	41.9 ✓ *	
A		—	50.0	.410	133		45.5 ✓ *	
Blank NH_3			50.0	.148 *				
Urea			50.0	.187 *	120 / .20 = .65 µg			

Blanks do not have the yellow-color intensity that the abundance samples. They would appear to be about half that of the samples.

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TITLE AGRICO - RESET

Project No. [illegible]
Book No. 82988-1

From Page No.

Sample Prep - ~~[illegible]~~ Set 5 1/8/79

Sample		Aliquot
In 1	M	5.0
	A	
Out 1	M	
	A *	
In 2	M	
	A	
Out 2	M	
	A *	
In 3	M	
In 3	A	5.0
Out 3	M	
	A	
In 4	M	
	A	
Out 4	M	
	A	
In 5	M	
	A	
Out 5	M	
	A	
In 6	M	
	A	
Out 6	M	
	A	
St 1	M	25.0
	A	
Blank Set 5		
St 2	M	25.0
	A	
St 3	M	
	A	
St 4	M	
	A	

* Urea Analysis - After NaOH treatment added - cannot be filtered because may have lost some material with ppt

* discard urea sample - some ppt lost when NaOH treatment added (no water added first!)

1/9/79

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Direct Nesslerization 1/8/79

Stock 1000 µg/ml NH_3 Dilute 10.0 mls → 500 mls ⇒ 20 µg/ml Working Solution

Tube total µg NH_3	mls W. Std in 50 ml Nessler tube	ABS (Read by SW Jr)
0	0	.00
20	1.0 ✓	.063
40	2.0 ✓	.105
100	5.0 ✓	.300
150	8.0 ✓	.49
200	10.0 ✓	.60

Sample	Dilution	Mls in Nessler Tube	original Sample Vol		Equivalent µg NH_3	total mg NH_3
#1 M	2→500.0	5.0	975 mls	✓.275	91	444
A				✓.29	96.5	470
#2 M			990 mls	✓.20	67	332
A				✓.22 → Bgd Blank	73 .00	361
#3 M			1100 mls	✓.20	67	368.5
A				✓.203	68	374
#4 M			970 mls	✓.22	73	354
A				✓.26	86.5	420
#5 M			1095 mls	✓.18	60.0	328.5
A		✓		✓.20	67.0	367
#6 M			1005 mls	✓.17	56.5	284
A				✓.186	62.0	312

						mg/ml NH_3
Unit 1 M	2→200	2.0 ✓		✓.33	✓109.5	5.48
A		2.0 ✓		✓.36	119.5	5.98 ✓
Unit 1 M		10.0 ✓		✓.31	103	1.03 ✓
A		5.0 ✓		✓.39	129.5	2.59
Unit 4 M		2.0		✓.279	92.5	4.62 ✓
A		2.0 ✓		✓.39	129.5	6.48 ✓
Unit 4 M		10.0 ✓		✓.26	86.5	0.86 ✓
A		2.0 ✓		✓.22 → Blank	73.0 .00	3.65 ✓

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✓ MAR 1-8-79		Recorded by	

TITLE AGRICO-RESET

Project No. [illegible]
Book No. 8823-1

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Prep of Sol 5

1/9/79

Sample Aliquot Diluted

Stock 5 M A 250

Stock 6 M A

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Project No. 82788-01
Book No. 82788-1 TITLE AGRICO - RESET

m Page No. ____ Neutralization of Set 2 - ammonia 1/11/79

Stock 1000 µg/ml NH_3 dilute 10.0 ml → 500 ml → 20 µg/ml NH_3 W.S.

tandard µg NH_3	ml W.S in 50.0 ml Neutralizer tube	Beginning Abs.	After Sample Abs @ 405 nm
0	0	.000	.000
20	1.0	.045	.032
40	2.0	.115	.092
100	5.0	.320 ✓	.309 ✓
160	8.0	.505	.490
200	10.0	.623 .620	.605

ammonia Analysis

	1st Dilution	2nd Dilution	Aliquot in Neutralizer tube	Abs.	%	µg NH_3	mg/ml NH_3	Retest
Set Samples								
1 M	5 → 250	none	1.0	.351	.345	110 µg	5.50	5.44
A				.338	.380	121.5 µg	6.08	6.02
2 M				.420 ✓	.412	132 µg	6.60	6.54
A				.392		125 µg	6.25	6.19
3 M				.185		59 µg	2.95	2.89
A				.265 ✓		84	4.20	4.14
4 M				.272		86.5	4.32	4.26
A				.390		124.5	6.22	6.17
5 M				.215 ✓		68.5	3.42 ✓	3.37
A				.270		86.0	4.30	4.24
6 M				.365		116.5	5.82	5.77
A				.360 ✓		115	5.75	5.69
Test Samples								
1 M		~~none~~	~~1.0~~	.470		150 µg	7.50	7.44
A				.542		173	8.65	8.59
2 M				.505 ✓		162	8.10	8.04
A				.475		152	7.60	7.54
3 M				.508		162	8.10	8.04
A				.565 ✓		181	9.05	8.99
4 M				.445		142	7.10	7.04
A				.482		153.5	7.68	7.62

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Std. 2 - NH_3 Calibration

Sample	Dilution	2nd Dilution	Aliquot	Abs.	Equivalent µg NH_3	mg/ml NH_3	Blank corrected Result mg/ml
5 M	5 → 250 ml	~~none~~	~~50~~ 10.0	.555	178 µg	8.90	8.84
A				.520	166	8.30	8.24
6 M				.595	191	9.55	9.49
A				.595	191	9.55	9.49

Stock Sample - NH_3

Sample	Sample Vol	Dilution	2nd Dilution	Aliquot	Abs.	µg	mg total NH_3	Blank corrected
1 M	975 ml	25.0-250	none	25.0	.233	90 µg	439	426
A					.005	Repeat below.		
2 M	990 ml				.182	58 µg	287	274
A					.003	Repeat below		
3 M	1100 ml				.210	67 µg	368.5	354
A					.210	67 µg	368.5	354
4 M	970 ml				.232	70.5	342	330
A					.225	72	349	337
5 M	1095 ml				.198	63	345	331
A					.222	70.5	386	372
6 M	1005 ml				.190	60.5	304	291
A					.192	61.0	306.5	294

Blank 2 NH_3	Reserve 250 ml	none	25.0	.135 (43)	Samples are cloudy, Abs reading reliable. Slightly above blank
Urea			25.0	.100 (32)	

→ = 32 µg ~~Abs~~ 25 ml

Matching curve for Spec 21 @ 405 nm

Distilled H_2O Both read 0.000

~~Blank~~ Solution Blank - Reader - adjust 1 to zero 0.000, 2nd read 0.000

200 µg NH_3 Standard Both read .623 Abs

~~Tube~~ Tube ID Blank I
Sample I

				Abs.	
Stock 1 A	25-250	—	50.0	.130	Both of these colors were as close to blank when the 200 µg was developed.
2 A			↓	.150	

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Reassignation of Set 2
Urea Samples

1/11/79

Omit Samples	1st Dilution	2nd Dilution	Aliquot in 50 ml	Mutitek Abs	×1.765 equivalent factor µg	mg urea/ml
1 m	5.0 → 250 ml	2.0 → 50.0	5.0	0.240	80.6	35.3
A				0.248	82.5	36.4
2 m				0.276	91.0	40.2
A				0.278	98.0	43.2
3 m				0.288	95.0	41.9
A				0.293	96.5	42.6
4 m				0.202	68.5	30.2
A				0.225	75.5	33.3
5 m				0.270	89.5	39.5
A				0.257	85.5	37.7
6 m				0.267	88.5	39.0
A				0.262	87.0	38.4
						mg urea/ml
Omitted 1 m	5.0 → 250 ml	1.0 → 50.0	1.0	0.365	116.0	521
A				0.368	119.0	525
2 m				0.324	106.0	468
A				0.330	107.5	474
3 m				0.350	114.0	503
A				0.348	113.0	499
4 m				0.338	110.0	485
A				0.344	112.0	494
5 m				~~0.355~~ 0.385	124.0	547
A				~~0.375~~ 0.380	122.5	540.5
Stock 1 m	Total Volume 25.0 → 250	none	Blank correction -12.8	10.0	0.154	54.0	Total mg urea 929	Blank 702
A	975 ml		-12.8	1.0 ml	0.348	113.0	1944	1922
2 m	990 ml		-12.8	10.0	0.176	61.0	107	842
A			-256	2.0	0.272	90.5	791	768
3 m	1,100 ml		-64	5.0	~~0.399~~ 0.400*	Dirty 135 µg	51.1	26.2
A					0.350*	114.9 µg	43	19.4
4 m	970 ml				0.500*	159 µg	54.4	32.5
A					0.600*	190	65.1	43.1
5 m	1095 ml				0.270*	89.5	34.6	9.9
A					0.235*	79.0	30.5	5.8

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Urea Std & Dilution		Dilution	Redilution	Blank Correction	Aliquot	Abs 725 nm	µg NH3 equivalent	mg Urea	Blank correct
Stock 1.005	M	25.0 → 250	none	-64 µg	50.0	.448	142.5	50.4	27.3
	A	↓	↓		↓	.305	100	35.5	12.8
								Urea mg/m2	
Outlet 5	M	5.0 → 250	1.0 → 50		1.0	.355	115.	507	
	A	↓	↓		↓	.378	121.	538	

STDS

µg NH3 in 50 ml Aliquot	Abs - Ref Standard	Abs Blank - Samples
0	.000	[illegible]
20	.048	.043
50	.105	.103
100	.312	.308
150	.505	.495
200	.640	.635

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Project No. 82938-01
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Nesslerization of Set 3 - Ammonia 1/12/79

Standards 1000 µg/ml NH_3 1 ml → 500 ml ⇒ 20 µg/ml Working solution

total µg NH_3	ml working sol'n 50 ml flask	Abs	
0	0	.000	
20	1	.058	.052
40	2	.128	.122
100	5	.330	.325
160	8	.523	.520
200	10	.680	.660

Sample	Dilution	2nd Dilution	ml in Nessler tube	Abs	Equivalent µg NH_3	µg/ml NH_3	µg/ml NH_3 Blank corrected
Inlet 1m	5.0 → 250 ml	none	1.0	.260	81	4050	3968
A				.358	111	5550	5468
2m				.348	107.5	5375	5293
A				.388	119.5	5975	5893
3m				.360	112	5600	5518
A				.374	115.5	5775	5693
4m				.172	54	2700	2618
A				.415	128	6400	6318
5m				.305	94.5	4725	4643
A				.340	105	5250	5168
6m				.280	87	4350	4268
A				.298	92	4600	4518
Outlet							
1m				.440	136	6800	6718
A				.470	144.5	7225	7143
2m				.440	136	6800	6718
A				.498	153.5	7675	7593
3m				.420	130	6500	6418
A				.595	183	9150	9068
4m				.470	144.5	7225	7143
A				[illegible]	196	9800	9718
5m				.405	125	6250	6168
A				.515	158	7900	7818
6m				.430	133	6650	6568
A				.453	140	7000	6918

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Book No. 82988-1

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Sample	Dilution	2nd Dilution	Ml in 50.0 ml Nesslerize	Abs.	Equivalent µg NH3	Total µg NH3	Total µg NH3 Blank Corrected
Stack Vol	25.0 → 250.	none	2.0				
1m 975 ml				.262	83	404.6	388.6
A				.315	98	477.8	461.8
2m 945 ml				.213	66.5	329.2	312.9
A				.225	71	351.5	335.2
3m 1100				.210	65.5	360.3	342.2
A				.230	72	396.0	374.0
4m 970				.230	72	349.2	333.2
A				.275	86	417.1	401.2
5m 1095				.185	58	317.6	299.6
A				.182	57	312.1	294.1
6m 1005				.165	51	256.3	239.8
A				.185	58	291.5	275.0
Blank 3 NH3	250 final Vol		25.0	.130	actually clear in color = 20 µg		

↳ = 41 µg

	Abs.
Blank 3 NH3	.130
Blank 3 NH3 centrifuged	.128
Bl 3 NH3 centrifuged at high speed ~10 min	.138

Blank Correction for Inlet + Outlet Samples p50

$$\mu g/ml\ NH_3 = \frac{\left(\text{equivalent } \mu g - \frac{41\,\mu g}{25\,ml} \times 1.0\,ml\right)}{1.0\,ml \text{ aliquot in Nesslerize}} \times \frac{250\,ml}{5.0\,ml \text{ distilled}}$$

Blank Correction Stack Sample p51

$$mg\ NH_3 = \frac{\text{equivalent } \mu g\ NH_3 - \frac{41\,\mu g}{25\,ml} \times 2\,ml}{2.0\,ml} \times \frac{250\,ml}{25\,ml \text{ aliquot}} \times \frac{\text{Sample volume } m^3}{} \times \frac{.001\,mg}{\mu g}$$

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Sample Prep (Set 4) 1/4/79

All Distillates Bulked to 2 liters

Sample		Aliquot
In 1	M	5.0 mL
	A	
Out 1	M	
	A	
In 2	M	
	A	
Out 2	M	
	A	
In 3	M	
	A	
Out 3	M	
	A	
In 4	M	
	A	
Out 4	M	
	A	
In 5	M	
	A	
Out 5	M	5.0
	A	
In 6	M	
	A	
Out 6	M	
	A	
~~Set 1~~	M	25.0
	A	
~~Set 2~~	M	
	A	
Set 3	M	
	A	
Set 4	M	
	A	

DISTILLATIONS

1/5/79

When Urea was distilled, these samples were light brown as compared to the black color of the others.

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From Page No. ____ Microlizgation - Set II p30 12/29/73

Ammonia - Inlet 2 mg/l solution Aliquot in some Nessler tube Abs
1 - M 10.0 mls
A
2 M
A
3 M
A
4 M
A
5 M
A
6 M
A

Ammonia - Outlet - Set -
1 - M 0.5 mls
A
2 - M
A
3 - M
A
4 - M
A
5 - M
A
6 - M
A

Blank 50.0

See P 46-48

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12-27/78

Urea-Inlet	2mL Solution	Acquin Mod Std	Abs
1-m A	2mL → 50.0	5.0	
2-m A			
3-m A			
4-m A			
5-m A			
6-m A			

Urea-Outlet		
1-m A	1mL → 50.0	1.0mL
2-m A		
3-m A		
4-m A		
5-m A		
6-m A		
Blank A		50.0

See p 46-48

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Sample Prep Set 2 12/27/76

Aliquot

Stack 1 $HgCl_2$ acid 25.0 mls

Stack 2 $HgCl_2$ acid

Stack 3 $HgCl_2$ acid

Stack 4 $HgCl_2$ acid

Stack 5 $HgCl_2$ acid

Stack 6 $HgCl_2$ acid

NH_3 + Urea Nitrates brought to 250 mls total volume

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Nesslerization Set 2 con't

Ammonia

aliquot in some Nessler tube

Sample

Stack 1	m	20.0 mls
	A	
2	m	
	A	
3	m	
	A	
4	m	
	A	
5	m	
	A	
6	m	
	A	

See p 46-48

Urea

Stack 1	m	10.0 mls
	A	
2	m	
	A	
3	m	50.0
	A	
4	m	
	A	
5	m	
	A	
6	m	
	A	

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Sample Prep - Set 3 1/12/79
All distillate Diluted to 250 ml

		aliquot
In 1	M	5.0 ml
	A	
Out 1	M	
	A	
In 2	M	
	A	
Out 2	M	
	A	
In 3	M	
	A	
Out 3	M	
	A	
In 4	M	
	A	
Out 4	M	
	A	
In 5	M	
	A	
Out 5	M	
	A	
~~Out 6~~	~~M~~	
	~~A~~	

1/3/79

In 6	M	5.0
	A	
Out 6	M	
	A	
Stack 1	M	25.0
	A	
Stack 2	M	25.0
	A	
Stack 3	M	
	A	25.0

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Sample Prep set 3 1/3/7[redacted]

		Weighed
Stock 4	m	25.0
	A	
5	m	
	A	
6	m	
	A	
Blank	3	

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Direct Nessler Method 1/3/79

Stock 1000 ppm NH_3 dilute 10.0 mls → 500 ml ⇒ 20 µg/ml NH_3

Std total	mls Working Solution	Abs	end
20 µg NH_3	1.0	.054	
	2.0	.102	
	~~3.0~~		
	5.0	.274	
	8.0	.458	.458
200	10.0	.548	

Samples		Sample vol.	2nd dilution	Sample vol.	Aliquot in Nessler Tube	Abs	Equivalent µg NH_3	total µg NH_3	µg/ml NH_3
1	M	975	2→500	975	5.0 mls	.244	96	419	
	A			0		.291	102	497	
2	M	990		990		.178	62	307	
	A					.188	66	327	
3	M	1100		1100		.186	65	355	
	A					.175	61.5	338	
4	M	970		970		.180	63.5	305	
	A					.206	72.0	349	
5	M			1095		.154	55.0	301	
	A					.164	58.0	318	
6	M			1015		.153	54.0	271	
	A					.158	56.0	251	
Rec H_2O			—		50.0				

							µg/ml NH_3
1	M	5→500	1.0	.143	51.0		5100
	A	5→500	1.0	.151	53.5		5350
1	M	5→500	5.0	.135	48.0		960
	A	5→500	5.0	.388	136.0		2720
4	M	5→500	1.0	.117	41.5		4150
	A	5→500	1.0	.163	59.0		5900
4	M	5→500	5.0	.124	44.0		880
	A	5→500	5.0	.607	211.0		4220

1 mg NH_3 = µg NH_3 analyzed × 1/mls Nessler tube × final vol. dilution / mls diluted × mls original volume sample × .001 mg/µg

mg/l = µg NH_3 analyzed × 1/mls Nessler tube × final vol. dilution / mls diluted

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TITLE AGRICO RESET

Project No. 33983-01
Book No. 33983-1

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Reclerization of Set 3 Urea's (cont'd) 1/12/79

Sample	Dilution	2nd dilution	aliquot of Neutralized	Abs	µg NH3	Urea mg/ml	Urea mg/ml Blank corrected
Stack	25.0 → 250	none	5				
4M	970		Blank Lowest -65	50.0	0.412 *	137	43.5	21.2
Acid					0.52 * 0.520	160	54.8	35.5
5M	1095				0.306 * 0.320	100	38.7	13.5
A					0.370 * 0.390	120	46.4	21.3
6M	1005				0.~~245~~ 0.254	75	27.7	4.61
A					0.~~160~~ adjust .168	52	18.4	<0

repeat 5M-6A

Blank Set 3 Urea 250 ml — 50.0 ~~500~~ rep. 42 = 65 µg

10.0 0.078 * = 24 µg

Blank Set 3 NH_3 250 — 2.0 0.012 = 4 µg

Standard

total µg NH_3	Abs	After Abs
0	0.000	0.000
20	0.072	0.072
40	0.125	0.125
100	0.322	0.320
160	0.520	0.520
200	.635	.630

Repeats

					Urea mg/ml
Inlet 5M	5 ml → 250	no 2nd dilution	10.0 ml	0.560 Abs	1.53

* Not visually the light in Abs.

1m Stack abs + visible check agree

				~ total mg
* 3m	visually	~ ~~30~~ 70	50-60 µg	25
3A	"	~	40-50 µg	17
4m	"	~	60 µg	21
4A	"	~	80 µg	27
5m	"	~	20 µg or less	8
5A	"	~	20 µg or more	8
6M	visually	~ 30 µg		~~10~~ 11
A	"	~ 10 µg		3.5

Blank 3 Urea 10 ml ~~app~~ visually looks like ~ 5 µg

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Calculations for Sets 2, 3, 4 + 5 ammonia + Urea

Ammonia Inlet + Outlet Samples

$$\mu g/ml \text{ Ammonia} = \frac{\mu g \text{ analyzed in Nessler tube}}{\text{aliquot mls in Nessler tube}} \times \frac{\text{final Vol 2nd dilution}}{\text{aliquot dilution}} \times \frac{250 \text{ mls Vol distilled}}{5.0 \text{ mls distilled}}$$

ammonia in Stack Samples

$$\text{total mg } NH_3 = \frac{\mu g \text{ analyzed in Nessler tube}}{\text{aliquot in Nessler tube}} \times \frac{250 \text{ mls final distillation Vol}}{25.0 \text{ mls distilled}} \times \text{Total Volume Sample mls} \times \frac{.001 \text{ mg}}{1 \mu g}$$

Urea Inlet + Outlet.

$$mg/ml \text{ Urea} = \frac{\mu g \, NH_3 \text{ analyzed}}{\text{aliquot in Nessler tube}} \times \frac{\text{2nd dilution Volume}}{\text{aliquot in 2nd dilution}} \times \frac{250 \text{ mls distilled}}{5.0 \text{ mls distilled}} \times 1.765 \times \frac{.001 \text{ mg}}{1 \mu g}$$

Urea - Stack Samples

$$\text{total mg Urea} = \frac{\mu g \, NH_3 \text{ analyzed}}{\text{aliquot in Nessler tube}} \times \frac{250 \text{ mls distilled}}{25.0 \text{ mls distilled}} \times \text{Total Volume Sample in mls} \times 1.765 \times \frac{.001 \text{ mg}}{1 \mu g}$$

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1/15/79

Realization Set 4 - Ammonia - Bump 43 for other samples

Standard 1000 ug/ml NH_3 10 ml → 500 ⇒ 20 ug/ml working solution

total ug NH_3	mls working soln in 50 ml Nessler	abs
0	0	.000
20	1	.051
40	2	.115
100	5	.324
160	8	.527
200	10	.650

Sample	Distillation	2nd dilution	mls Nessler tube	abs	Equiv. ug NH_3	ug/ml NH_3	Plant Control see p.
Inlet 2M	50 → 250 mls	none	1.0	.379	118.5	5925	5353
A				.400	125	6250	6175
3M				.389	121.5	6075	6003
A				.370	116	5800	5723
5M				.338	106	5300	5228
A				.381	120	6000	5929
6M				.282	88.5	4425	4353
A				.339	106	5300	5223
Outlet 2M				.520	162	8100	8029
A				.558	173.5	8675	8605
3M				.391	122.5	6125	6053
A				.486	151.5	7575	750[redacted]
5M				.422	132	6600	6528
A				.392	122.5	6125	605[redacted]
6M				.518	161.5	8075	8003
A				.464	145	7250	717[redacted]
						Total mg NH_3	
Stack 2M	25.0 → 250		2.0	.191	60.5	299.5	295[redacted]
A				.212	66.5	329.2	315[redacted]
3M				.184	58	319	303.[redacted]
A				.211	66.5	365.8	350[redacted]
5M				.169	53.5	292.9	277.[redacted]
A				.190	60	328.5	312[redacted]
6M				.167	53	266.3	252.0

Total vol: 990 mls; 1100 mls; 1095 mls; 1005 mls

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1/16/79

Nesslerization of Set 4 - Urea - See p 42 for other samples

Standard (~~[illegible]~~ 100 ug NH_3/ml NH_3 10 ml → 500 ml ⇒ 20 ug/ml working soln

Total ug NH_3	mls working soln into 50 ml flask	Abs	
0	0	.000	
20	1	.050	.038
40	2	.129	.115
100	5	.330	.330
160	8	.542	.540
200	10	.680 vs	.680

x1.765 urea factor

Sample	Distillation	2nd dilution	mls into Nessler tube	Abs	~~add 1 ml 4N NaOH to each tube~~ EQUIV vs NH3	mg urea
Inlet 2M	5.0 → 250 ml	2.0 → 50 ml	5.0	.340	100.5	44.3
A				.330	98	43.2
3M				.320	95	41.9
A				.320 vs	95	41.9
5M				.280	83	36.6
A				.285	85	37.5
6M				.295	88	38.8
A				.285 vs	85	37.5
Outlet 2M		1.0 → 50 ml	1.0	.342	.101	445.7
A				.350	104	458.9
3M				.448	132.5	584.7
A				.372 vs	110.5	487.6
5M				.372	110.5	487.6
A				.373	111	489.8
6M				.391	116.5	514.1
A				.417 vs	123.5	544.9
Tank 2M	25.0 → 250 ml	~~none~~	10.0 (Total vol 9.90 ml)	.193	57.5	100.5
A			10.0	.189	56	97.9
3M			50.0 (1100 ml)	.500	148	57.5
A			50.0	.538 vs	159	61.7
5M			(1095 ml)	.539	159.5	61.7
A				.339	100	38.7
6M			(1105 ml)	.560 vs	166	58.9

Total mg urea

* 7.0 NaOH added → 99.6; 190 → 57; 80 → 24.4

Witnessed & Understood by me, | Date | Invented by * Ron made first adding 4N NaOH. Ron blank was | Date | Recorded by

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~~Neutralization of Set 5 - ammonia~~ 1/17/79

Neutralization of Set 4 - Urea (cont'd)

Notes on P56 1/16/79

1) In an attempt to decrease ~~turbidity~~ turbidity in Urea samples added 1 ml of 4N NaOH to each nessler tube after pipetting aliquot + bringing up to 50 ml w/H_2O.
2) also made up controls of Stock 2M, 2A and distilled H_2O and did not add 4N NaOH.
3) All samples did not look turbid all compared well with color of standards.
4) When I read controls in (2) above - they read virtually identically to regular samples (with NaOH) see *
5) Conclusion - in this analysis - apparently - the NaOH did not make difference. - Tomorrow - will run samples ST 3M + 3A over + see what happens - with + w.o. NaOH addition

Blank Correction

a Blank was not run with set 4 ~~data~~ samples. Use the average of Blanks run with sets 2, 3 & 5 for Set 4 Blank Correction

Blank	$\mu g NH_3$/ml in Nessler tube	page
2	1.28	47
3	1.64	51
5	1.36	59

average Correction for NH_3	1.43 µg/ml sample
	71.5 µg/50 ml

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Page No. ___ Nesslerization of Set 5 - Ammonia 1/17/79

Standard 1000 ug/ml NH_3 10 ml → 500 ml ⇒ 20 ug/ml working soln

Total NH_3 (ug)	mls working soln in 50 ml Nessler tube	Abs	
0	0	.000	
20	1	.049	.051
40	2	.114	.120
100	5	.315	.318
160	8	.515	.510
200	10	.635	.638

Sample	Pipetted	2nd dilution	Blank Corrected Sample	ml into Nessler	Abs	Equiv. ug NH_3	not Blank corrected ug/ml NH_3
Inlet	5.0 → 250 ml	none		1.0			
1M			4407 ug/ml NH_3		.283, ~~.350~~	89.5	4475
A			5457		.350, ~~.320~~	110.5	5525
2M			4982		.320, ~~.380~~	101	5050
A			5932		.380	120	6000
3M			5407		.348	109.5	5475
A			4382		.282	89	4450
4M			4082		.264	83	4150
A			6582		.423	133	6650
5M			5132		.330	104	5200
A			5232		.335	106	5300
6M			3282		.212	67	3350
A			5182		.332	105	5250
Outlet							
1M			6007 ug/ml		.385	121.5	6075
A			6982		.448	141	7050
2M			6832		.439	~~.25~~ 138	6900
A			7082		.454	143	7150
3M			5982		.383	121	6050
A			6232		.400	126	6300
4M			6282		.402	127	6350
A			7332		.470	148	7400
5M			6982		.448	141	7050
A			7307		.462	145.5	7275

cont'd

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Page No. 58 Set 5 - Ammonia cont'd

1/17/79

Sample	Distillation	2nd dilution	Stand. curve	ml into Nessler	Total Volume sample ml	abs	Eq. µg/ml NH3	Total mg NH3
Outlet 6M	5.0 → 250ml	none	6632	1.0		.425	134	670
A	↓		3757	↓		.562	Vo 176.5	882.5
Stack 1M	25.0 → 250ml		430 mg NH3	2.0	975	.287	91	443.6
A			505		975	.339	107	521.6
2M			175		990	.120	38	188.1
A			333		990	.222	Vo 70	346.5
3M			316		1100	.131	42	231
A			364		1100	.219	69	379.5
4M			207		970	.141	45.5	220.7
A			343		970	.232	Vo 73.5	356.5
5M			199		1095	.121	39	213.5
A			330		1095	.198	63	344.9
6M			185		1005	.122	39.5	198.5
A			318		1005	.208	Vo 66	331.7
Blank NH3	final Vol 250ml	none		25ml	abs	.106	34	

not Blank corrected

p58 Blank correction

$$\text{Inlet + Outlet } \mu g/ml = \frac{\text{Equivalent } NH_3 - \left(\frac{34\,\mu g}{25\,ml} \times \text{ml Sample in Nessler tube}\right)}{\text{original nessler tube}} \times \frac{250\text{ ml dilution}}{5.0\text{ ml distillate}}$$

p54 Blank correction Calculation

$$\text{total mg } NH_3 = \frac{\left(\text{Equivalent } \mu g - \frac{34\,\mu g}{25\,ml} \times 2\,ml\right)}{2.0\text{ ml in nessler tube}} \times \frac{250\,ml}{25\,ml} \times \text{Sample Volume} \times \frac{.001\text{ mg}}{\mu g}$$

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Project No. 82138-01
Book No. 82138-1 TITLE AGRICO - RESET

Page No. ____ 1/18/79

Nesslerization of Set 5 - Urea

Standard 1000µg/ml NH_3 10 ml → 500 ml ⇒ 20 µg/ml NH_3 working soln

Total NH_3 (µg)	mls work. soln in 50 ml Nessler tube	abs	
0	~~mls~~ 0	.000	.000
20	1	.057	.052
40	2	.155	.151
100	5	.~~316~~ 361	.362 ✓o
160	8	.590	.579
200	10	.710 ✓	.710

before adding Nessler reagent added 1 ml 4N NaOH to each tube

Sample	Distillation	2nd dilution	mls into Nessler	abs	Equiv. µg NH_3	mg/ml Urea
Inlet 1M	5.0 ml → 250	2.0 → 50.0	5.0	0.315	89	39.3
A	↓	↓	↓	.300	84.5	37.3
2M				.394	110	48.5
A				.360	101	44.6
3M				.352 ✓o	99	43.7
A				.352	99	43.7
4M				.280	79	34.9
A				.380	106.5	47.0
5M				.320 ✓o	90	39.7
A				.320	90	39.7
6M				.328	92	40.6
A				.342	96.5	42.6
Outlet 1M		1.0 → 50.0 ml	1.0	.448 ✓o	125	551.6
A				.450	~~19~~ 125.5	553.8
2M				.398	111.5	492.0
A	no sample		No sample			
3M				.411	115	507.4
A				.425 ✓o	119	525.1
4M				.341	96	423.6
A				.381	106.5	469.9
5M				.423	118.5	522.9
A				.412 ✓o	115.5	509.6
6M				.440	123	542.7
A				.413	116	511.9

cont'd

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Neesterization of Sets - Urea (Cont'd)

1/18/79

~~Sample~~	Distillation	2nd dilution	mls sets	Nessler	abs	µg NH3	[redacted]
~~Stack~~ 1M	25.0 → 250ml	none	10.0	975	.213	60	[redacted]
A				975	.191 ✓o	54	[redacted]
2M				990	.210	59	103
A				990	.183	52	[redacted]
3M			50.0	1100	.439	122.5	[redacted]
A				1100	.424 ✓o	118.5	[redacted]
4M				970	.605	169	[redacted]
A				970	.596	166	[redacted]
5M				1095	.337	94.5	[redacted]
A				1095	.323 ✓o	91	[redacted]
6M				1005	.578	161	[redacted]
A				1005	.500	139.5	[redacted]
Blank ~~Set~~ 5 Urea	250ml		~~10.0~~ 25.0		.089	~~28~~ 26	
Stack - set ~~4~~ 5 Urea							
NO ~~H_2SO_4~~ * 3M	25.0 → 250		50.0		.228 ✓o	64	
4N NaOH * A			50.0		.239	67	
~~Stack~~ O(3)					.000		

1/30/79 mm

Blank Correction

Stack Samples

25ml = 26µg

∴ 50ml = 52µg

10ml = 10.4µg

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APPENDIX C.2

LABORATORY SAMPLE PRESERVATION

* Threshold = 3.5

LAB UREA SAMPLES

AGRICO-2

Sample no.	Date	F_D	obs.	X_1 (mg NH_3/sample)	C (mg NH_3/sample)	ppm (µg/ml) (X_1-C) $\frac{50}{25}$ x1.765 (UREA ONLY)
a NH3	1/21/79	—	.000	0	0	0
NH3.D	"	2.5	.175	61	17	2.2
urea	"	2.5x5	.252	83.5	3.6	35.3
b		—	.000	0	0	0
		2.5	.188	65	17	2.4
		2.5x10	.325	104.5	1.8	96.6
c		—	.008	3.0	4.0	0*
		2.5	.110	42	13	2.1
		2.5x5	.258	85	3.6	35.9
d		—	.010	3.5	4.0	0*
		2.5	.112	43	13	2.2
		2.5x10	.352	112	1.8	97.2
e		—	.005	2.0	0	0
		2.5	.090	37	37	0.2
		2.5x5	.252	83.5	3.6	35.3
f		—	<0	0	0	0
		2.5	.222	74.5	13	2.1
		2.5x10	.325	104.5	1.8	90.6
a NH3						—
NH3.D	1/26	2.5	.080	22	40.5	0
urea	1/26	2.5x5	.298	87	6	34.9
b						—
		2.5	.146	40	40.5	0
		2.5x10	.365	108	3	92.7
c						—
		2.5	.090	24.5	11.5	0.7
		2.5x5	.290	84.5	3.8	35.6
d						—
		2.5	.132	36	11.5	1.2
		2.5x10	.355	105	1.9	91.0
e						—
		2.5	.088	24	19.0	0.3
		2.5x5	.290	84.5	3.3	35.8
f						—
		2.5	.162	44.5	19.0	1.3
		2.5x10	.370	110	1.7	95.6

DATE	F_D	obs.	X_1	C	ppm
					—
1/29	2.5	.075	20.5	9.5	0.6
1/29	2.5x5	.315	91	4.4	38.2
					—
	2.5	.140	38	9.5	1.4
	2.5x10	.375	109	2.2	94.3
					—
	2.5	.085	23	8	0.8
	2.5x5	.315	91	5.2	37.9
					—
	2.5	.145	39.5	8	1.6
	2.5x10	.380	110	2.6	94.8
					—
	2.5	.085	23	11	0.6
	2.5x5	.310	90	3.6	38.1
					—
	2.5	.175	49	11	1.9
	2.5x10	.372	108	1.8	93.7
1/31	—	.022	6.0	0	0.1
1/31	2.5	.106	31	32	0
1/31	2.5x5	.315	91	5	37.9
	—	.030	8.0	0	0.2
	2.5	.186	56	32	1.2
	2.5x10	.372	108	2.5	93.1
	—	.018	5.0	0	0.1
	2.5	.232	67.5	11.5	2.8
	2.5x5	.304	88.5	3.6	37.5
	—	.025	7.0	0	0.1
	2.5	.150	43.5	11.5	1.6
	2.5x10	.370	107.5	1.8	93.7
	—	.032	9.0	0	0.2
	2.5	.118	34	27.5	0.5
	2.5x5	.308	89.5	4	37.7
	2	<0	0	0	0
	2.5	.232	67	27.5	2.1
	2.5x10	.378	109.5	2	94.9

DATE	F_D	obs	X_1	C	ppm
2/2/79	—	.022	6.5	4.2	0
2/2	2.5	.090	26	19	0.4
2/2	2.5x5	.280	80	2.9	34.0
	—	.040	12.0	4.2	0.2
	2.5	.162	47	19	1.4
	2.5x10	.330	94	1.5	81.6
	—	.002	0	8.5	0
	2.5	.084	27.5	7.5	0.9
	2.5x5	.292	92.5	2.2	35.9
	—	.018	5.5	8.5	0
	2.5	.135	39	7.5	1.6
	2.5x10	.376	99	1.1	86.4
	—	.014	4.0	0	0.1
	2.5	.088	25.5	13	0.6
	2.5x5	.282	80.5	2.7	34.3
	2	<0	0	0	0
	2.5	.202	58.5	13	2.8
	2.5x10	.370	106	1.4	92.3
2/5/79	—	.026	7	1.5	0.1
2/5	2.5	.098	28	13.5	0.7
2/5	2.5x5	.277	85	1.6	36.8
	—	.072	20.5	1.5	0.4
	2.5	.155	44.5	13.5	1.6
	2.5x10	.340	104.5	0.8	91.5
	—	.040	11.5	0	0.2
	2.5	.064	47	21	1.3
	2.5x5	.285	88	1.9	38.0
	—	<0	0	0	0
	2.5	.146	41.5	21	1.0
	2.5x10	.342	105	1.0	91.8
	2	<0	0	3	0
	2.5	0.097	21	9.5	0.6
	2.5x5	.268	83	1.2	36.1
	2	<0	0	3	0
	2.5	0.220	63	9.5	2.7
	2.5x10	.340	104.5	0.6	91.7

UREA LAB SAMPLES

AGRICO 2

Sample no.	Date	F_0	abs.	X_1	C	ppm
a	NH_3 2/1/75	—	.010	3.5	0	0.1
	$NH_3 \cdot D$ 2/1/75	2.5	.070	24	9	0.8
	UREA 2/1	2.5x5	.312	89.5	3.4	77.6
b		—	.040	13.5	0	0.3
		2.5	.150	48	9	2.0
		2.5x10	.365	104	1.7	90.3
c		—	<0	0	0	0
		2.5	.075	26	0	1.3
		2.5x5	.320	91	2.9	38.9
d		—	<0	0	0	0
		2.5	.145	47	0	2.4
		2.5x10	.374	107	1.5	93.1
e		2	<0	0	0	0
		2.5	.056	17	6	0.6
		2.5x5	.308	87.5	2.8	37.4
f		2	<0	0	0	0
		2.5	.170	64	6	2.9
		2.5x10	.370	105.5	1.4	91.9

Date	F_0	abs.	X_1	C	ppm
2/9	—	.052	14.5	4.5	0.3
2/9	2.5	.134	38	14	1.2
2/9	2.5x5	.290	86	2.2	37.0
	—	.090	25	4.5	0.1
	2.5	.222	63	14	2.5
	2.5x10	.359	106	1.1	92.6
	—	.020	5.5	9	0.2
	2.5	.090	25	8	0.9
	2.5x5	.310	92	1.7	39.8
	—	.018	5	9	0.2
	2.5	.176	49.5	8	2.1
	2.5x10	.358	106	0.9	92.8
	2	<0	0	0	0
	2.5	.090	25	10	0.8
	2.5x5	.296	88	2.3	37.8
	2	.012	3	0	0.1
	2.5	.160	45	10	1.8
	2.5x10	.316	94	1.2	81.9

Date	F_0	abs.	X_1	C	ppm
2/12	—	0.050	15	19.5	0
2/12	2.5	.116	34.5	12	1.1
2/12	2.5x5	.300	89	3.8	37.6
	—	.092	28	19.5	0.2
	2.5	.215	64	12	2.6
	2.5x10	.355	105.5	1.9	91.4
	—	.014	5	39	0
	2.5	.072	22	4	0.9
	2.5x5	.312	93	6.6	38.1
	—	.020	6	39	0
	2.5	.170	51	4	2.4
	2.5x10	.375	111	3.3	95.0
	2	<0	0	0	0
	2.5	.068	20.5	10.5	0.5
	2.5x5	.310	92	4	38.8
	2	<0	0	0	0
	2.5	.140	42	10.5	1.6
	2.5x10	.374	111	2	96.2

m Page No. ____ Preparation of 6 Urea Samples 1/24/79
for Stability studies

Standards to be analyzed ~~always~~ once every 2 days for Urea & NH_3 for 20 days

a 40 mg Urea/l H_2O
b 100 mg Urea/l H_2O
c 40 mg Urea/l H_2O with 2 ml sat. $HgCl_2$ solution added
d 100 mg " /l H_2O " 5 ml sat $HgCl_2$ " added
e 40 mg Urea/l H_2O with 2 ml conc H_2SO_4 added.
f 100 mg Urea/l with 5 ml " " "
Blank H_2O + 5cc H_2SO_4/l H_2O = Bl-A
Blank-M = H_2O + 5 cc $HgCl_2$/l - Bl-M

Prepare 2 liters of each solution. Add preservative before diluting up to 2 liter line.

Prepare a Stock solution of 10.0 g/l Urea = 10 mg/ml Urea

40 mg/l Standards use 8 mls of Stock → 2 l
100 mg/l " " 20 mls of Stock → 2 l

Ammonia & Urea Distillation 1/24/79

Sample	aliquot	distilled Volume Urea + NH_3
a	100 mls	250 mls
b	↓	↓
c	↓	↓
d	↓	↓
e	↓	↓
f	↓	↓
Bl-A	↓	↓
Bl-M	↓	↓

Note - samples which contained $HgCl_2$ turned brown when the sodium thiosulfate declorinating agent was added

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Set ① Oday 1/25/79

Direct Nesslerization of Samples a – f and Bl M + Bl A

Stock 1000 µg/ml – Dilute 5 ml → 250 → 20 µg NH_3/ml – Working solution

Standards (from MMF 6p 28-29)

total µg NH_3	mls WS in 50 ml	Abs	Abs after
0	0.	.000	.000
20	1.	.058	.052
40	2.	.136	.130
60	3.	.204	.195
80	4.	.405	.400
100	5.	.342	.338
300	10.	.685	.660

Limit of detection = $\frac{3.5\,\mu g}{50\,ml}$ = .07 µg/ml (0.01 abs)

< .07 mg/l NH_3

Samples	aliquot		
a	50.0 ml	.000	nd
b		.000	n.d
c		.008	n.d
d		.010	n.d
e		.005	n.d
f	25.0 + NaOH	< .000	n.d
Bl A	25.0 + NaOH	< .000	n.d
Bl m	50.0	.012	(n.d)

Distilled Samples Set 1 Oday

NH_3	Aliquot in Nessler tube	Abs		Equivalent µg	µg/ml NH_3	corrected for Blank & µg/ml NH_3
a (distilled 100 → 250)	50.0	.175	vis 20 µg	62	3.1	1.45
b		.188		65	3.25	1.60
c		.110		43	2.15	0.50
d		.112		44	2.2	0.55
e		.090		37	1.85	0.20
f		.222	vis 5 µg	75	3.75	2.1
Bl A		.075	(2-5 µg)	33	1.65	0
Bl M		.000	(zero)	0	< .15	

µg/ml NH_3 = $\frac{\mu g}{50.0\,ml} \times \frac{250\ \text{distilled vol}}{100\ \text{ml distilled}}$

Avg for a, b

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1/25/79

Urea	aliquot in Nessler tube Dilution		Abs	Equivalent µg	mg/2 Urea mg/ml	Blank correction µg	µg/ml Urea Blank Correction
a	100 ml → 250 ml 10.0	120 µg	.257	84	37.1	-3.6	35.48
b	5.0		.325	105	92.7	-1.8	91.07
c	10.0		.258	85.5	37.7	-3.6	36.14
d	5.0		.325	105	92.7	-1.8	91.07
e	10.0		.252	84	37.1	-3.6	35.48
f	5.0		.325	105	92.7	-1.8	91.07
Be A	50.0		.028	18	1.6		
Be M	50.0		.028	18	1.6		

$$\mu g/ml\ Urea = \frac{(\mu g - Be)}{aliquot} \times \frac{250\ ml\ diluted\ final}{100\ ml\ aliquot\ diluted} \times 1.765$$

Standard

0 total µg/ml	ml of 20 µg/ml	.000	.000
20	1	.034	.030
40	2	.100	.094
60	3	.170	.162
80	4	.240	.230
100	5	.300	.295
160	8	.515	.505
200 µg	10	.660	.650

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Page No. ____ (Set 2) (2 days) 1/26/79

Distill a-f & Bl A & Bl M as on p. 61 100 ml aliquot to 250 ml (absorbed in 50 ml Boric acid solution.)

Distill

Bl with H_2O → 250 ml (Boric acid)
100 ml - absorbed in H_2O only.

1/29/79

Analysis of Set 2
NH_3 - Distiller.

Sample	aliquot in Nessler tube	Abs	Equivalent µg NH_3	mg/l NH_3		mg/l NH_3 Blank corrected
a	50.0 ml	.080	22	1.1	-2.0	<0
b		.146	40	2	-2.0	0
c		.090	24.5	1.22	-.58	.64
d		.132	36	1.8	-.58	1.22
e		.088	24	1.2	-.95	.25
f	~~25.0~~ 50.0	.162 ov	44.5	2.22	-.95	1.27
Bl A	~~25.0~~ 50.0	.070	19.0	0.95		0
Bl M	50.0	.042	11.5	0.56		0
Bl H_2O - Boric acid	50.	.150	41.5	2.07		
Bl H_2O - H_2O	50.	.070	19.0	0.95		

				mg/l Urea		mg/l Urea Blank corrected
a	10.0	.298	87	38.4	-2.6	35.8
b	5.0	.365	108	95.3	-2.6	92.7
c	10.0	.290	84.5	37.3	-1.7	35.6
d	5.0	.355	105	92.7	-1.7	91.0
e	10.0	.290	84.5	37.3	-1.5	35.8
f	5.0	.370	110	97.1	-1.5	95.6
Bl A	50.0	.062	15	1.5		
Bl M	50.0	.070	19.0	1.7		
Bl H_2O/Boric	50.0	.110	30	2.6		
Bl H_2O/H_2O		.032	8.5			

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1/29/79

Set 3 distilled NH_3 Sample

	Aliquot	Abs	equivalent µg NH_3	mg/l NH_3 not Blank corrected	Blank Correction	Blank Corrected Result
a	50.0 mls	.075	21.5	1.075	-.48 * mg/l	0.545 mg/l NH_3
b		.140	38.0	1.9	-.48 *	1.42
c		.085	23	1.15	-.40	0.75
d		.145	39.5	1.975	-.40	1.575
e		.085	23	1.15	-.55	0.60
f		.175	49	2.45	-.55	1.90
Be A		.042	11	.55		
Be m		.030	8	.40		

* Blank correction for a + b is average of Be A + Be m

Standards total µg in 50 mls NH_3	Abs	Abs after
0	.000	.000
20	.072	.068
40	.145	.142
100	.340	.340
160	.530	.530
200	.650	.645

Calculation

$$mg/l\ NH_3 = \frac{(eq\ \mu g)}{aliquot} \times \frac{250\ ml\ vol\ distilled}{100\ ml\ distilled}$$

mg/l Urea = above × 1.765

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E AGRICO - RESET

Project No. [illegible]

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Page No. Soil Samples - Set 3 (5 days) 1/27/79

Prepare Samples from p 63. 100 ml aliquots distilled to 250 ml.
NH_3 + Urea

Prepare Samples from p 63 100 ml aliquots distilled 1/31/79
to 250 ml for NH_3 + Urea - Set 4 (7 days)
also do ~~the~~ sample a and sample c using 25 ml aliquots. Then
analyze for urea using 50 ml in nessler tube (look for cloudiness).

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Book No. 82788-1 TITLE AGRICO - RESET

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Analysis of Set 3 Urea and Set 4 Samples 1/31/79

Standards	ilr	aft
0 total µg NH_3	.000	
20	.075	.068
40	.138	.130
100	.342	.338
160	.545	.54
200	.695 ov	.69

Samples - Direct NH_3 1-31-79 (Set 4)	aliquot	Abs		Equivalent µg NH_3	mg/l NH_3 not Blank correct
a	50	.022		6	.12
b	50	.030		8	.16
c	50	.018		5	0.10
d	50	.025		7	0.14
e	50	.032 ov		9	0.18
f	25.0 + NaOH	<.000		0 <.1	0
BeA	25.0 + NaOH	<.000	usually appear the same - slightly above 0	0	0
BeM	50	.040		Equivalent µg 11µg	.22

Distilled NH_3 - (Set 4)	ml distilled ≈ 250 ml	aliquot	Abs	Equivalent µg NH_3	mg/l NH_3	Blank Correction	corrected mg/l NH_3
a 100 ml	100 → 250	50.0	.106	31	1.55	-1.6	0
b			.186	54	2.70	-1.6	1.1
c 100 ml			.232	67	3.35	-.58	2.77
d			.15 (~30µg)	435	2.18	-.58	1.6
e			.118	34	1.70	-1.22	.48
f			.232 ov	67	3.35	-1.22	2.13
BeA			.085 (5-10µg)	245	1.22		
BeM			0.040 (3-10µg)	115	0.58		
Be H_2O			0.11 (~10µg)	32	1.6		
a - 25 ml	25.0 → 250		.094 (min ~12µg)	27	5.4	-1.6	3.8
b - 25 ml	25.0 → 250		.210 (min ~17µg)	61	12.2	-.55	11.6

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1/31/79

-Urea - Set 3-					Equiv. µg NH3	mg/l Urea	Blank Corrected	Blank Corrected mg/l Urea
	mls distilled	aliquot	Abs	mx µg				
a	100 → 250	10.0	.315	80-90	91.0	40.15	-2.16	37.99
b		5.0	.375	~100	109.0	96.19	-2.16	94.03
c		10.0	.315		91.0	40.15	2.56	37.59
d		5.0	.380		110.0	97.08	-2.56	94.52
e		10.0	.310		90.0	39.71	-1.54	38.12
f		5.0	.372 o/		108	95.3	-1.54	93.72
B2A		50.0	.062	5µg	18	1.59		
B2M		50.0	.090	5µg	26	2.56		
					22			

Urea Set 4								
	mls distilled → 250	aliquot	Abs					
a 100	100	10.0	.315		91.0	40.15	-2.16	37.99
b		5.0	.372		108	95.31	-2.16	93.15
c 100		10.0	.304		85.0	38.23	-1.54	37.24
d		5.0	.370		107.5	94.87	-1.54	93.28
e		10.0	.308		89.5	39.49	-1.81	37.68
f		5.0	.378 o/		109.5	96.63	-1.81	94.82
B.A		50.0	.072	5µg cl	20.5	1.81		
B2 M		50.0	.064	5 cl	18	1.59		
B2 H_2O		50.0	.085	10 cl	24.5	2.16		
a_{25}	25.0	50.0	.325	80-90 old	15	40.60	-2.16	38.44
c_{25}	25.0	50.0	.570	80-90 old	65.5	46.24	-1.54	44.65

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Lab-Urea Sampler - Set 5 - 9 days 2/2/79

Distill NH_3 then do Kjeldahl analysis for Urea for samples on p63.
- Stability study a, b, c, d, e, f, BeA, BeM, BeH2O 100 ml aliquots distilled to 250 mls.

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TITLE AGRICO - RESET

From Page No. ____ Nesslerization of Distilled NH_3 + Direct NH_3 of Set 5 2/3/79

Standards	Abs
0 ~~ml~~ µg NH_3	.000
20	.068
40	.135
100	.350
160	.550
200	.680

Direct NH_3 - Set 5	aliquot	Abs	Equivalent µg NH_3	mg/l NH_3 not blank corrected	Blank correction	corrected results mg/l NH_3
a	50.0 ml	.022	6.5	0.13	–	0.13
b	↓	.040	12.0	0.24	–	0.24
c	↓	.002	nd	<.06	0.17	<.06
d	↓	.018	5.5	0.11	0.17	nd (<.06
e	↓	.014	4.0	0.08	–	.08
f	25.0 ml → N-04	<0 or	nd	<.12	–	<.12
BeA	25.0 ml → N-04	<0	nd	<.12		
BeM	50.0 ml	.030	8.5	0.17		

Distilled NH_3 - Set 5	aliquot	Abs	visual	Equivalent µg NH_3	mg/l NH_3 not blank corrected	Blank correction	corrected results mg/l NH_3
a	100 ml → 250 50.0 ml	.090		26.0	1.3	-.95	.35
b	↓ ↓	.162		47	2.35	-.95	1.4
c	↓ ↓	.084		24.5	1.22	-.38	0.84
d	↓ ↓	.135		40.0	2.0	-.38	1.62
e	↓ ↓	.088		25.5	1.28	-.65	0.63
f	↓ ↓	.202		59.0	2.95	-.65	2.30
BeA	↓ ↓	.045	~5 µg	13.0	0.65		
BeM	↓ ↓	.026	~5 µg	7.5	0.38		
Be H_2O	↓	.066	~10 µg	19.0	0.95		

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From Page No. — Set 6 (12 days) 2/5/79

Prepare Sampler from p 63 100 ml aliquot distilled to 250 ml for both NH_3 and Urea

Nesslerization of Set 5 Urea, Set 6 Direct NH_3 and set 6 Distilled NH_3

Standards Stock 1000 µg/ml NH_3. Dilute 10.0 ml → 500 ml ⇒ 20 µg/ml NH_3 Working Solution

Standards total µg NH_3	ml WS in 50 ml Ness Tube	Abs.	and also
0	0.0	.000	
20	1.0	.060	.052
40	2.0	.132	.125
100	5.0	.355	.350
160	8.0	.560	.555
200	10.0	.695	.690

Set 5 Urea

Sample	Distillation	aliquot in Ness. Tube	Abs	Equivalent µg NH_3	mg/l Urea not Blank corrected	Blank correct	Result Blank corrected mg/l Urea
Set 5 Urea	100 ml → 250						
a		10.0	0.280	80.0	35.3	-1.3	34.0
b		5.0	0.330	94.0	83.0	-1.3	81.7
c		10.0	0.292	84.0	37.1	-1.0	36.1
d		5.0	0.346	99.0	87.4	-1.0	86.4
e		10.0	0.282	80.5	35.5	-1.2	34.3
f		5.0	0.370	106	93.5	-1.2	92.3
BlA		50.0	.048	13.5	1.2		
BlM		50.0	.040	11.5	1.0		
$Bl H_2O$		50.0	.052	14.5	1.3		

Calculation

$$\text{mg/l Urea} = \frac{\text{Eq µg } NH_3}{\text{aliquot ml}} \times \frac{250}{100} \times 1.765$$

$\frac{145.2 \cdot 9}{5}$ $\frac{1.5 \cdot 1.5}{10}$

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2-5-79

Samples	Dilution	Aliquot in Neut. tube	Abs.		Equivalent µg NH_3	mg/l NH_3	Blank corrected	mg/l NH_3 corrected
Set 6 - Distill NH_3	none	50.0	~~.026~~		~~7.0~~			
a			.026		7.0	0.14	–	0.14
b			.072		20.5	0.41	–	0.41
c			.040		11.5	0.23	-.06	.17
d			≈ 0	min ~5µg	nd < 3µg	< .06	-.06	nd < .06
e		25.0	< 0		nd < 3µg	< .12		< .12
f		25.0	< 0		nd < 3µg	< .12		< .12
BQA		25.0	.000		n.d < 3µg	< .12		
BQM		50.0	.012		3µg	0.06		
Distilled NH_3 Set 6 a	100 ml → 250	50.0	.093		28	1.4	-.7	0.7
b			.155		46	2.2	-.7	1.5
c			.064		18.0	0.9	-1.05	n.d
d			.146		42	2.1	-1.05	1.05
e			.074		21	1.05	-.5	0.55
f			.220		63	3.15	-.5	2.65
BQA			.034	} value about 5µg	10	0.5		
BQM			.075		21	1.05		
BH_2O			.048		13.5	0.7		

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Project No. 82988-01
Book No. 82988-1 TITLE AGRICO - RESET

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2/7/79

Prepare Set 7 (14 days) Lab Urea Sample
100 ml aliquots of a-f BLA, BLM, & BLH2O
distilled to 250 ml

Nesslerization of Set 6 Urea, Set 7 Direct NH_3
Distilled NH_3

Standards 1000 µg/ml NH_3 Stock dilute 10 ml → 500 ml ⇒ 20 µg NH_3/ml Working Solution

total µg NH_3	ml of W.S	abs	corr
0	0	.000	.008
20	1	.048	.046
40	2	.124	.108
100	5	.328	.332
160	8	.520	.520
200	10	.650	.650

Set 6 Urea

Sample	dilution	Aliquot in ml	abs	Equivalent µg NH_3	mg/l Urea not Blank corrected	Blank correction	mg/l Urea corrected
a	100→250	10 ml	.274	85	37.5	-.7	36.8
b		5 ml	.340	104.5	92.2	-.7	91.5
c		10.	.285	88	38.8	-.8	38.0
d		5.	.342	105	92.7	-.8	91.9
e		10	.268	83	36.6	-.5	36.1
f		5	.340	104.5	92.2	-.5	91.7
BLA		50	.020	6.0	0.5		
BLM		50	.030	9.5	0.8		
BLH2O		50	.024	8.0	0.7		

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2/7/79

Sample	distillation	aliquot in ml	abs	Equivalent µg NH_3	mg/l NH_3 not Blank corrected	Blank correction	Result mg/l NH_3 corrected	
Set 7 Direct NH_3	none	50.0						
a			.010	4.0	.08	—	.08	
b			.040	12.5	0.25	—	.25	
c			<0 .088	6.0	0.12	—	.12	
d			<0 ~5µg .005	<4.0	<.08	—	<.08	
e		25	<0 *	<4.0	<.16	—	<.16	
f		25	<0	<4.0	<.16	—	<.16	
BOA		25	<0	<4.0	<.16	—	<.16	
BOM		50	<0 0	<4.0	<.16	—	<.16	
Set 7 Distilled NH_3								
a	100-250	50.0	.07	11.0	.55	-.45	0.10	
b			.15	48.0 48	2.4	-.45	1.95	
c			.075	26.0	1.3	<.2	<1.3	
d			.145	47.0	2.35	<.2	<2.35	
e			.056	17.0	0.85	0.3	.55	ck jmm
f			.170	54.0	2.7	0.3	2.4	
BOA			.018	6.0	0.3			
BOM			.000	nd<4	<.2			
BOA-O			.025	9.0	.45			

* [redacted] µg std reads 0.122 Abs

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Book No. 82733-1 TITLE AGRICO-RESET

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2/9/79

Set 8-Lab Urea Samples (16 days)

100 mls aliquots of a-f Bl A, Bl M & Bl H_2O - Diluted with H_2O to 250 ml volume & Urea to 250 mls volume

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TITLE AGRICO-RESET

Project No. 25723-01
Book No. S2988-1

Item Page No. —

analysis of Set 7 Aliq and Set 8 Direct NH_3, Distilled NH_3 + Blks

2-9-79

Standards	mls 20 µg/ml NH_3	abs	and
0 ~~total~~ µg NH_3	0	.000	.000
20	1	.076	.072
40	2	.145	.140
100	5	.352	.350
160	8	.55	.545
200	10	.665	.665

Sample	Distillation	aliquot	abs		Equivalent µg NH_3	mg/l NH_3 not blank corrected	Blank correction	mg/l NH_3 Blank corrected
Set 8 Direct NH_3	none	~~50.~~						
a		50.0 mls	.052	ov	14.5	0.29	—	.29
b			.090		25.5	0.51	—	.51
c			.020		5.5	0.11	-.12	nd 0
d			.018		5.0	0.10	-.12	nd 0 <.1
e		25.0	ne<0		<2.5	<.1	-.10	<.1 nd .01
f			.012	ov	3	0.12	-1.0	0.02 <.1
Bl A			<0		<2.5	<.10		
Bl M		50.0	.032		6.0	0.12		
Distilled NH_3								
a	100 mls → 250 mls	50.0 mls	.134		36.0	1.9	-.7	1.2
b			.222		63.0	3.15	-.7	2.45
c			.090		25.5	1.28	-.4	0.88
d			.176		50.0	2.5	-.4	2.1
e			.090		25.5	1.28	-.5	0.78
f			.160	ov	45.0	2.25	-.5	1.75
Bl A			.036		10.0	0.5		
Bl M			.030		8.0	0.4		
Bl H_2O			.050		14.0	0.7		

To Page

Witnessed & Understood by me,	Date	Invented by	Date
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Project No. 82788-01
Book No. 82788-1 TITLE AGRICO - RESET

From Page No. ____

2-9-79

Sample Set 7 Urea	Dilution	aliquot	abs.	Equivalent µg NH_3	mg/l Urea not Blank corrected	Blank correction	mg/l Urea Blank corrected
a	100 ml → 250.	10.0	.317	83.5	39.0	-1.5	37.5
b	↓	5.0	.365	104	91.8	-1.5	90.3
c	↓	10.0	.320	91	40.2	-1.3	38.9
d	↓	5.0	.374 ov	107	94.4	-1.3	93.1
e	↓	10.0	.308	87.5	38.6	-1.2	37.4
f	↓	5.0	.370	105.5	93.1	-1.2	91.9
Bl A	↓	50.0 ~~10.0~~	.050	14.0	1.20		
Bl m	↓	50.0	.052	14.5	1.30		
Bl H_2O	↓	50.0	.060	17.0	1.50		

Set 8 Urea			
a	100 → 250	10.0	not done today
b	↓	5.0	
c	↓	10.0	
d	↓	5.0	
e	↓	10.0	
f	↓	5.0	
Bl A	↓	50.0	
Bl m	↓	50.0	
Bl H_2O	↓	50.0	

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Project No. 82-155-01
Book No. 82-155-1 TITLE AGRICO - RESET

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Sample Prep, Sed & Cont 1/5/79

Sample	Aliquot ~~Double~~
St5 M A	250
St6 M ~~A~~ not done	↓

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		Recorded by	

Project No. 82733-01
Book No. 82733-1 TITLE AGRICO - RESET

From Page No.

Nesslerization of Set 3 - Urea 1/12/79

	Distillation	2nd dilution ml	ml in Nesslerization	Abs @ 445 nm	Equivalent ug NH3	mg/ml Urea
Inlet						
1 M	5.0 ml → 250	2.0 → 50.	5.0	0.264	82	36.2
A				0.262	81.5	36.0
2 M				0.306	95	41.9
A				0.310	96	42.4
3 M				0.316	97.5	43.0
A				0.320	100	44.1
4 M				0.240	~~68~~ 74.5	32.9
A				0.225	70	30.9
5 M				0.038 o Repeat p53	Abs. = .560 = 173	1.53
A				0.285	88	38.8
6 M				0.282	87.5	38.6
A				0.285	88	38.8
Outlet		1.0 → 50	1.0	~~0.382~~	~~118~~	~~520.7~~
1 M				~~0.394~~ .382	118	~~536~~ 520.7
A				0 ~~.252~~ .394	121.5	~~481.0~~ 536.1
2 M				0.352	109	~~459.0~~ 481.0
A				0.338	104	~~489.8~~ 459.0
3 M				0.360	111	~~527.3~~ 489.8
A				0.388	119.5	527.3
4 M				0.348	107.5	474.3
A				0.345	106.5	469.9
5 M				0.375	116	511.8
A				0.372	115.5	509.6
6 M				0.402	124	547.2
A				~~0.400~~ .398	123	~~542.2~~ 542.7
Stock	25.0 → 250 ml					
1 M	975	none	Blank correction -.13	10.0	0.215 * OK recalculation	67.5 / 1162	93.8
A			-.13	10.0	0.158	58 / 99.8	77.4
2 M	990		-.13	10.0	0.194	60 / 104.8	82.0 ?
A			-.13	~~5.0~~ 10.0	0.244	76 / 132.8	110.?
3 M	1.00		-.15	5.0	0.420 *	45 / 50.3	25.0
A			-.15		0.265 *	92 / 31.8	6.6

Cont

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Page No. 2/12/77

Prepare (Set 9) Urea sub sample 19 days
a-f Bl A, Bl M, Bl H_2O
100 mls distilled into 250 mls for NH_3 & Urea
(from pp 30-32 q.m.m. #6)

Nesslerization of Set 8 Urea and Set 9 Direct NH_3, Distilled NH_3 and Urea

Standards total µg NH_3	mls of 20 µg/ml NH_3 Working Solution	Abs. Before	Abs. after
0	0	.000	.000
20	1	.064	.062
40	2	.135	.130
100	5	.350	.350
160	8	.545	.540
200	10	.680	.675

Sample	Distillation	Aliquot in 50 ml Nesslerizer	Abs	Equivalent µg NH_3	mg/l Urea not Blank corrected	Blank correction	mg/l Urea Blank Corrected
Set 8 Urea							
a	100 mls → 250 mls	10.0	.290	86.0	37.9	-1.0	36.9
b	↓	5.0	.358	106.	93.5	-1.0	92.5
c	↓	10.0	.310	92	40.6	-0.8	39.8
d	↓	5.0	.358	106	93.5	-0.8	92.7
e	↓	10.0	.296	88	38.8	-1.1	37.7
f	↓	5.0	.316	94	83.0	-1.1	81.9
Bl A	↓	50.0	.038	12	1.06		
Bl M	↓	↓	.028	8.5	0.8		
Bl H_2O	↓	↓	.035	11	1.0		

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Project No. 82788-01
Book No. 82788-1 TITLE AGRICO - RESET

From Page No. 83

Nesslerization con't 2-12-79

Sample	Distillation	ml in Nessler Tube	Abs	Equivalent µg NH_3	mg/l NH_3 not Blank correct	Blank correction	mg/l NH_3 Blank Corrected
Set 9 Direct NH_3							
a	none	50.0	.050	15.	0.3	–	.3
b			.092	28	0.56	–	.56
c			.014	5.0	0.10	-.78	nd
d			.020	6.5	0.13	-.78	nd
e		25.0	<.000	<3.5	<.14	-.14	nd
f			<.000	<3.5	<.14	-.14	nd
Bl A			<.000	<3.5	<.14		
Bl M		50.0	.130 * ov	39.	.78		
Set 9 Distilled NH_3							
a	100 → 250 ml	50.0	.116	35.	1.75	-.6	1.15
b			.215	64.	3.2	-.6	2.6
c			.072	22.	1.1	-.2	0.9
d			.170	51	2.55	-.2	2.35
e			.068	20.5	1.02	-.52	.50
f			.140	42	2.1	-.52	1.58
Bl A			.034	10.5	0.52		
Bl M			.012	4.0	0.20		
Bl H_2O			.040	12.0	0.6		

* false Abs reading - usually looks like 0 to 5 µg NH_3

To Pa

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Nesslerization Cont'd 2-12-79

Sample	Distillation	aliquid in 50 ml Nessler tube	Abs		Equivalent µg NH_3	mg/l Urea not Blank corrected	Blank correction	mg/l Urea Blank Corrected
Set 9 Urea								
a	100 → 250 ml	10.0	.300		89.5	39.5	-1.7	37.8
b	↓	5.0	.355		105.5	93.1	-1.7	91.4
c	↓	10.0	.312		92.5	40.8	-2.9	37.9
d	↓	5.0	.375		111.	98.0	-2.9	95.1
e	↓	10.0	.310		92.0	40.6	-1.8	38.8
f	↓	5.0	.374		111	98.0	-1.8	96.2
BeA	↓	50.0	.066	reading OK	20.0	1.8		
BeM	↓	↓	.110		33	2.9		
BeHgO	↓	↓	.062		19.5	1.7		
BeM repeat	↓	↓	.115					

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APPENDIX D

AMMONIA INTERFERENCE ON UREA ANALYSIS

NH3 INTERFERENCE

Project No. 82785-01 Tech. Dir. #2

Book No. MF-6 TITLE EPA Proj # 79-NHF-13, Work assignment 11

Page No. 3-28-79

Prepare 220 mL of of color reagent
- 4.00 g p-dimethylaminobenzaldehyde
- + 200 mL 95% ethyl alcohol
- + 20 mL HCl.

2 Urea Standard Solution 2 mg urea / mL H_2O

0.2000 g of urea → 100 mL with H_2O

Bottle of urea - Baker Analyzed Reagent 302-4976 (on side of bottle)

3-29-79

3 20 mg NH_3 / mL H_2O 31.4100 g NH_4Cl → 500 mL H_2O

wt of NH_4Cl	31.4100		31.4100
wt of Beaker	51.2000	wt Beaker	117.6000
	82.6100 g		149.0100

Sample #	mL Urea Std	actual Urea mg/mL	mL NH_3 std	actual mg/mL NH_3	Total Vol	Abs	After Sample Abs	Results mg/mL Urea	Rates to actual mg/mL
Blank	0 mL	0	0 mL	0	0	.000	.000		
1	5	0.1	0	0	100	~~.176~~ .169	.170		
2	5	0.05	0	0	200	~~.091~~ .091	.091		
3	15	0.15	0	0	200	0.258	.260		
4	10	0.20	0	0	100	0.356	.357		
5	10	0.10	1	0.10	200	.175 or .176		0.101	1.01
6	10	0.10	5	0.50	200	0.172		0.102	1.02
7	5	0.10	5	1.00	100	0.~~174~~ or .181		0.106	1.06
8	5	0.10	25	5.00	100	0.~~228~~ 223		0.130	1.30
9	5	0.10	50	10.00	100	0.263		0.151	1.51

To Page No. 63

Witnessed & Understood by me, Date Invented by Date

From Page No. 62

Calculate Molarities of Samples on p62 3-24-78

Molecular Wht of Urea is 60g Molar Solution = 60 mg/ml

Molecular wht of ammonia is 17g Molar Solution = 17 mg/ml

Sample	Molarity of Urea	Molarity of NH_3	Ratio $\frac{\text{Molarity } NH_3}{\text{urea}}$	
1	.00167	0	0	
2	.00083	0	0	
3	.0025	0	0	
4	.0033	0	0	
5	.00167	.00588	3.52	1.01
6		.0294	17.60	1.02
7		.0588	35.21	1.06
8		.294	176.0	1.50
9		.588	352.1	1.51

According to the article (Watt, George W. and Joseph D Chrisp, "Spectrophotometric Method for Determination of Urea", Analytical Chemistry, 26: 452-453, 1954)

"Ammonium Chloride does not interfere when present in a 10 to 1 Mole ratio and introduces only 1% relative error when the mole ratio is 15 to 1."

To Page

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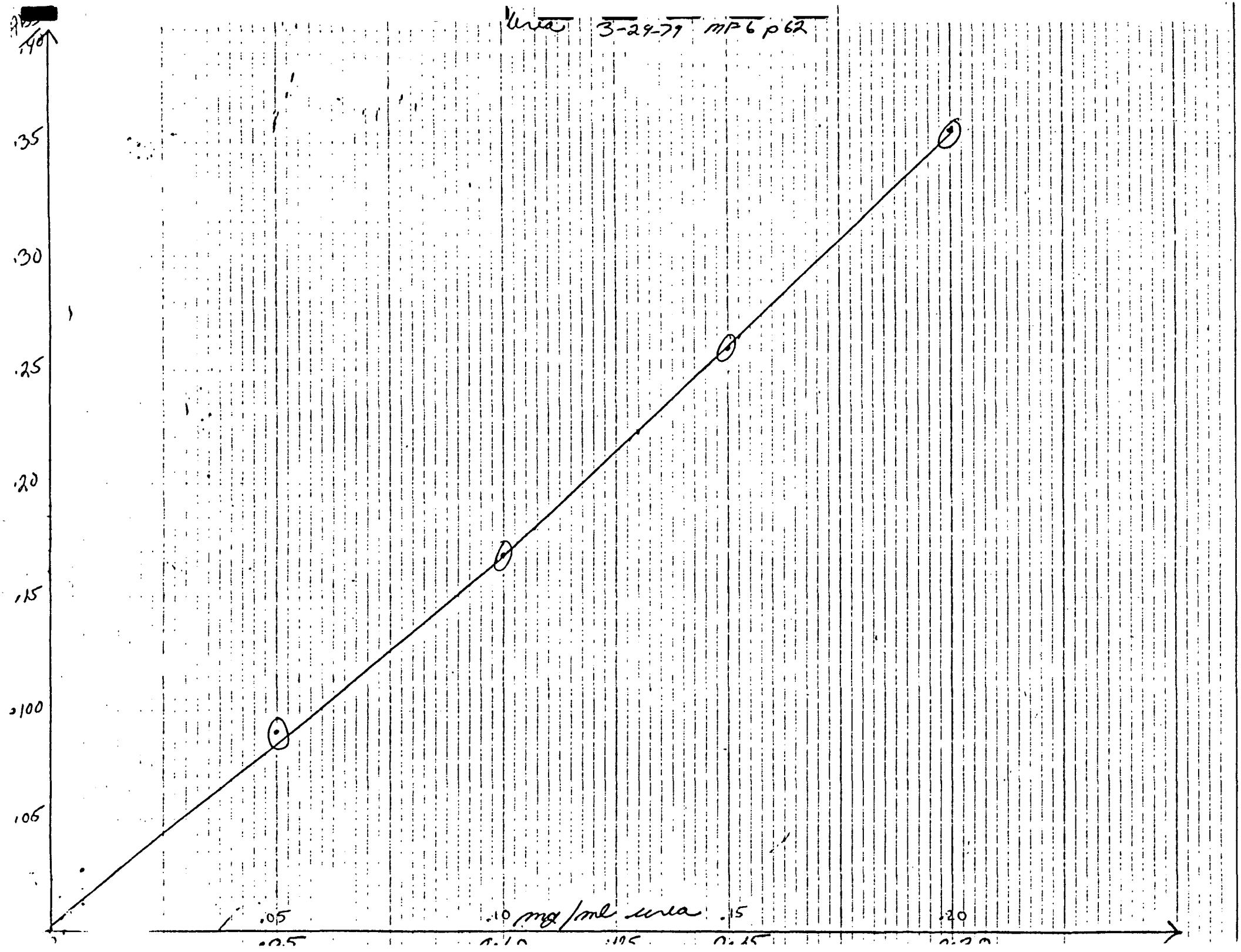
Urea 3-29-79 MP6 p62



TR[redacted] THE [redacted]ARCH [redacted]ORPO[redacted]ATION [redacted] NEW [redacted]LAND[redacted]

Report of Chemical Analysis of Non-Routine Samples

Client: EPA

Contract No: 82988-01

Reviewed by:

Report to: WAW

Laboratory No: 143-29 (3)

Date Received: 3-20-79

Date Reported: 3-30-79

Type Sample: Filter _____ Fuel Oil _____ Sediment _____ Impinger _____ Other Lab Standards

Sample Number	Location	Analysis No. 1	Analysis No. 2	Analysis No. 3	Analysis No. 4	Analysis No. 6	TLV
	Abs	actual mg/ml Urea	analytical Result mg/l Urea	actual mg/ml NH_3		Molar Ratio NH_3/Urea	
Blank	.000	0.00	std	0		0	
1	.169	0.10	std	0		0	
2	.091	0.05	std	0		0	
3	.258	0.15	std	0		0	
4	.356	0.20	std	0		0	
5	.170	0.10	0.101	0.10		3.5	
6	.172	0.10	0.102	0.50		17.6	
7	.181	0.10	0.106	1.00		35.21	
8	.223	0.10	0.130	5.00		176	
9	.263	0.10	0.151	10.00		352	
Limit of detection for 0.005 absorbance = .003 mg/ml							

Analyzed by: [illegible]

INTER-OFFICE COMMUNICATION

TO: WAW | OFFICE

FROM: MMF | OFFICE

SUBJECT: EPA 82788-01 Work Assignment 11 | DATE: 3-30-94

MESSAGE:

Will, I have attached an article that explains the NH_3 interference into a molar ratio of 15:1. Samples 5 and 6 seem to agree.

SIGNED: Marge

REPLY

DATE | SIGNED

ZO-8

ORIGINATOR: DETACH THIS COPY. SEND REMAINING SET, CARBON INTACT, FOR USE OF REPLIER.

were prepared and will be discussed elsewhere. The first four of these derivatives give blue or blue-green colors in strong acid solution. Apparently the specificity of the analytical procedure depends on the formation of the pyrazinophenazine under the given conditions. If the derivatives are isolated first (*2*), many of them form highly colored products in strong acid solution.

ACKNOWLEDGMENT

This work was supported by research grants from the National Heart Institute and National Microbiological Institute. It is a pleasure to thank Otto Schales for samples of 2,3-butanedione, 4,5-octadione, and the ethanedial bisulfite compound and for criticism of the manuscript. Thanks are due to Thomas B. Crumpler for his suggestions concerning the preparation of the manuscript. A sample of hypophosphorous acid received from the Oldbury Electro-Chemical Co. is acknowledged with thanks.

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RECEIVED for review July 22, 1953. Accepted December 7, 1953.

Spectrophotometric Method for Determination of Urea

GEORGE W. WATT and JOSEPH D. CHRISP
The University of Texas, Austin, Tex.

The work described in this paper was done to provide a dependable method for the determination of urea in samples containing urea, hydrazine, semicarbazide, and ammonium ion. This method involves a spectrophotometric determination of urea and is based upon the yellow-green color produced when *p*-dimethylaminobenzaldehyde is added to urea in dilute hydrochloric acid solution. This system exhibits a transmittancy minimum at 420 mμ and shows good agreement with Beer's law at urea concentrations up to 320 p.p.m. With the instrument and procedure used, a relative error of only 1% is realized over the optimum urea concentration range of 50 to 240 p.p.m. Interferences investigated include ammonium ion, hydroxylamine, hydrazine, and semicarbazide; the latter two interfere, but a procedure for their removal is given. Although developed for the analysis of a particular type of sample, this method should be readily adaptable to the determination of urea in a wide variety of samples.

IN A recent communication, the present authors described a spectrophotometric method for the determination of hydrazine (*4*) that is based upon the use of *p*-dimethylaminobenzaldehyde to develop yellow-colored solutions having a transmittancy minimum at 458 mμ. In the course of certain studies in which this method was employed for the determination of hydrazine, it became necessary to analyze numerous samples not only for hydrazine, but also for semicarbazide and urea, all in the presence of appreciable concentrations of ammonium ion. Spectrophotometric determination of hydrazine followed by determination of hydrazine and semicarbazide by the iodate titration method of Jamieson (*3*) permitted the determination of semicarbazide by difference. However, the existing methods for the determination of urea were either clearly inapplicable or failed to give satisfactory results when used in the analysis of samples of known urea content.

From an inspection of Figure 2 in the previous paper (*4*), it is evident that the broad transmittancy minimum region exhibited by solutions containing urea and *p*-dimethylaminobenzaldehyde might serve as a basis for the development of a satisfactory method for the determination of urea. Further experiments have shown that this system exhibits a reproducible transmittancy minimum at 420 mμ, which has been utilized in the manner described below for the determination of urea in samples of the type already indicated.

EXPERIMENTAL

Apparatus. A Beckman Model DU spectrophotometer and matched Corex cells of 1.001-cm. light path were used for all transmittancy measurements. The instrument was operated at constant sensitivity using a slit width of 0.1 mm., corresponding to a nominal band width of 2.4 mμ at 420 mμ.

Materials. Urea (Baker's C.P. analyzed) was recrystallized twice from methanol, washed with diethyl ether, and dried in vacuo for 48 hours over anhydrous magnesium perchlorate; melting point, 132° C., corrected. Hydrazine dihydrochloride (Eastman No. 1117) and semicarbazide hydrochloride (Eastman No. 226) were titrated by the Jamieson method (*3*), and the purity was found to be 99.8 and 99.4%, respectively. Potassium iodate (Merck ACS reagent grade) and *p*-dimethylaminobenzaldehyde (Eastman No. 95) were used as received. All other materials employed in this work were reagent grade chemicals that were used without further purification.

Standard Urea Solution. This solution was prepared by dissolving 0.4 gram of urea in distilled water and diluting to 100 ml. Aliquots of this solution were used to make up the various urea solutions from which different aliquots were used to develop colored urea solutions within the concentration range 16 to 4[illegible] p.p.m.

Color Development. The color reagent used was the same that employed in the method for the determination of hydrazi-

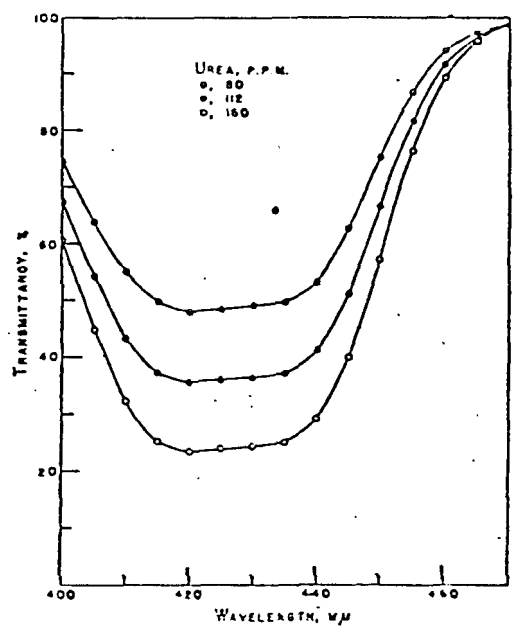

Figure 1. Spectral Curves for Urea with *p*-Dimethylaminobenzaldehyde

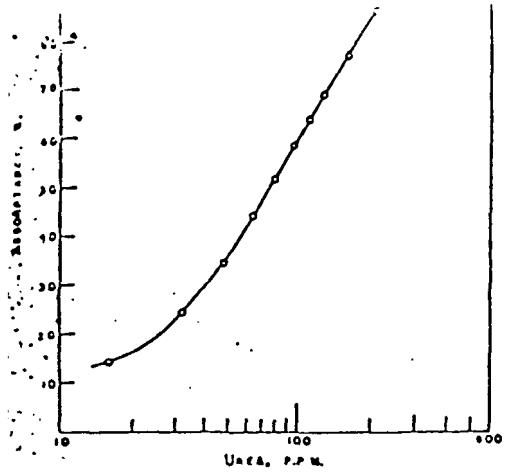

Figure 2. Calibration Curve for Urea with p-Dimethylaminobenzaldehyde at 420 mμ

(4), except that 95% ethyl alcohol was employed instead of absolute ethyl alcohol. [Although absolute alcohol was specified for use in the determination of hydrazine (4), it has since been found that 95% ethyl alcohol is equally satisfactory.] This color reagent consists of: p-dimethylaminobenzaldehyde (2.000 grams), 95% ethyl alcohol (100.0 ml.), and concentrated hydrochloric acid (10.0 ml.). Ten milliliters of color reagent were added to appropriate urea aliquots, and this mixture was diluted to a total volume of 25.0 ml. with distilled water. Blanks consisted of 10.0 ml. of the color reagent diluted with distilled water to a total volume of 25.0 ml.

Properties of the Color System. Upon addition of the color reagent to solutions containing urea, the yellow-green color develops immediately at room temperature and is stable after 10 minutes. Color-developed solutions of urea varying in concentration from 80 to 160 p.p.m. showed no detectable change in transmittancy in 11 days. These same solutions had a temperature coefficient of 0.6% absolute transmittancy per 1° C. over the range 20° to 40° C.; this effect was completely reversible. (In all of the urea determinations carried out in these laboratories, the samples were maintained at 25° in a thermostat attached to the spectrophotometer.)

When 11 ml. of color reagent were used, rather than 10 ml. for a given concentration of urea, the per cent transmittancy decreased 3.5%. Freshly prepared color reagent and color reagent that had aged for 1 week gave identical results.

If the acid concentration of color-developed solutions (normally 0.44*M* in hydrochloric acid) is increased by 0.1*M*, the per cent transmittancy is increased 1.5%. Samples having the same acid concentration showed an average deviation of 0.07% absolute transmittancy for urea concentrations over the range 80 to 160 p.p.m.

In Figure 1, the plot of per cent transmittancy versus wave length shows a transmittancy minimum at 420 mμ. The colored system follows Beer's law up to urea concentrations of 320 p.p.m.

Analysis of Samples of Known Composition. Following numerous preliminary experiments, five samples of urea weighing between 0.2 and 1.0 gram were used to prepare samples for analysis by this method. The urea concentrations were unknown to the analyst; the collective analysis errors were 1.6, −1.0, −0.9, −0.3, and 1.1%.

Interferences. A brief study of the extent to which hydroxylamine, ammonium chloride, hydrazine, and semicarbazide interfere with this determination was made by adding known quantities of these substances to solutions containing urea at a concentration of 120 p.p.m. when analyzed. As the concentration of hydroxylamine is progressively increased, the transmittancy minimum is shifted from 420 to 410 mμ when the mole ratio of hydroxylamine to urea is 8 to 1; however, the presence of hydroxylamine in a mole ratio as great as 10 to 1 leads to only a 1% relative error. Ammonium chloride does not interfere when present in a 10 to 1 mole ratio and introduces only a 1% relative error when the mole ratio is 15 to 1. Urea cannot be determined by this method when either semicarbazide or hydrazine is present in a 1 to 1 mole ratio.

Urea solutions that are highly acidic may be analyzed satisfactorily if they are first neutralized with sodium hydroxide to the [illegible] concentrations of [illegible].

Procedure. For the determination of hydrazine, semicarbazide, and urea in solutions containing all three of these substances, the following procedures were employed: An appropriate aliquot was analyzed for hydrazine by the method of Watt and Chrisp (4). Another aliquot was taken for the determination of total hydrazine and semicarbazide by the method of Jamieson (3) and the semicarbazide content was obtained by difference. The residual solution from the Jamieson iodate titration was treated as follows. Since the iodine monochloride formed during the iodate titration interferes with the urea determination, it was removed by titration with standard sodium thiosulfate solution using the disappearance of the characteristic color of iodine in the chloroform layer as the end point. The resulting solution (ca. 4*M* in hydrochloric acid) was neutralized with sodium hydroxide to the phenolphthalein end point, after which 2 or 3 drops of 1*M* hydrochloric acid were added to dissipate the indicator color. The aqueous phase was separated, the chloroform layer was washed once with 10 ml. of water, the aqueous solution and washings were made up to a known volume, and aliquots were taken for subsequent color development and spectrophotometric determination of urea.

Six standard samples containing urea, semicarbazide hydrochloride, and hydrazine dihydrochloride were thus analyzed for urea over the working range of concentration at 420 mμ; the relative error in the urea determination did not exceed 4% in any case. In a typical instance involving determination of all three components by the procedures outlined above, a sample was known to contain 0.187 gram of hydrazine, 0.603 gram of urea, and 0.688 gram of semicarbazide; the values found by analysis were 0.185, 0.616, and 0.692, respectively.

DISCUSSION

The calibration curve employed in this work is shown in Figure 2, in which per cent absorbance (100 − per cent transmittancy) is plotted against the logarithm of the concentration of urea expressed in parts per million. The inflection point in the curve occurs at 63% absorbance (urea at a concentration of 110 p.p.m.), and the slope of the curve at this point corresponds to a maximum relative error of 2.7% per 1% absolute photometric error, in agreement with Beer's law (1). The working range of concentration of urea is 50 to 240 p.p.m. for a 4% relative error per 1% absolute photometric error; these limits were determined as described by Ayres and Young (2). The absolute photometric error can be kept down to 0.25% with good temperature control; hence the relative analysis error should not be greater than 1.0% for this concentration range.

Particular care should be exercised in making up and adding the color reagent, as significant errors are introduced by small differences in the quantity of color reagent in blank and unknown. The true optimum quantity of color reagent for use in this method was not established in the present studies owing to the fact that the color reagent has a maximum absorption wave length at 415 mμ. As stated above, however, use of more than the specified quantity of color reagent results in a decrease in transmittancy presumably owing to absorption attributable to the color reagent; the use of lower concentrations of this reagent was not investigated.

Although this method was developed for use in the analysis of a particular type of sample, the nature of the method is such that it should be readily adaptable to the determination of urea in a wide variety of samples.

ACKNOWLEDGMENT

The authors wish to express their gratitude to G. H. Ayres for his interest and assistance.

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Received for review November 2, 1953. Accepted December 28, 1953. This work was supported by the U. S. Navy Bureau of Ordnance, Contract N123s-67363, Task Order 2.

APPENDIX E

EVALUATION OF STANDARD PROCEDURES FOR PROPOSED EPA UREA ANALYTICAL METHOD

Includes:

E.1 Effect of Preliminary Distillation
E.2 Sulfuric Acid Interference

APPENDIX E.1

EFFECT OF PRELIMINARY DISTILLATION

8-28-79
MMT-A

Analysis of Urea Audit Sample

NH_3 is a known interference in the p-dimethylaminobenzaldehyde colorimetric method. The ~~method~~ modified urea method first boils off the NH_3 at pH 9.5 with Borate Buffer. The residue in the flask is then diluted to 100.0 mL and analyzed. - Take an aliquot, add 10 mL color reagent, dilute to 25.0 mL and read @ 420 nm.

The audit samples were boiled along with a series of standards

A series of standards were made up directly (no boiling)

The audit samples were calculated twice, based on each type of standards

Also for my own information I ran the audit samples directly (no boiling) and calculated them based on the direct standards

Gary McAllister Phone# 1-919-541-2237

AUDIT SAMPLES - W.R. GRACE - AUGUST 1979

Five urea-in-mannitol audit samples were analyzed as a quality assurance check. Samples were weighed, then dissolved in 100 mls of water and analyzed for urea according to the preliminary ammonia distillation, p-dimethylamino-benzaldehyde colorimetric procedure. Samples were also analyzed by the direct colorimetric procedure. The distilled samples were also read against the direct standards to determine whether it was necessary to distill the standards.

Excluding sample #4, the errors for the distilled samples and standards and the direct samples and standards were within the 5% tolerance allowed. The distilled samples analyzed against direct standards were approximately 14% lower than the actual value. It was decided to do a preliminary ammonia distillation on both samples and standards followed by the colorimetric procedure for this project.

R[redacted] of C[redacted]al A[redacted] of [redacted] Routi[redacted]mple[redacted]

[redacted]

Client: W R Grace, Memphis, Tn EPA

Contract No: 0488-E80-10

Reviewed by: [illegible]

Report to: [illegible]

Laboratory No: 401-79(*)

Date Received: 8-27-79

Date Reported: 8-30-79

Type Sample: Filter _____ Fuel Oil _____ Sediment _____ Impinger _____ Other Audit Sample

Sample Number	actual Urea concentration	diluted/distilled sample/standard	Relative Error*	distilled filtrate	Relative Error*	direct filtrate	Relative Error*
Audit 1	26.56%	26.27	1.09%	23.98	13.48%	26.33	0.87%
2	48.00%	45.40	4.38%	40.2	16.25%	45.5	5.21%
3	41.96%	42.80	2.00%	37.1	11.58%	40.8	2.76%
4	9.92%	11.70	17.94%	10.3	3.83%	12.6	27.0%
5	19.998%	19.3	3.49%	17.2	13.94%	20.0	0.01%
	* per EPA	5% Tolerance allowed.					

Analyzed by: [illegible]

Form [illegible]012

TITLE WRD Lab, Memphis, Tn — Project No. — Book No. LPG

From Page No. TRC - Audit Samples 8-27-79

Per Gary McAllister - weigh the total amount of sample in each vial.
Dilute contents to 100.0 mls

Pipet 25.0 mls into 1L flask and distill off NH_3.

Prepare a series of standards to ~~be distilled~~ have NH_3 boiled off
- Stock 5.00 g/l Urea - 5 mg/ml

Standard total mg/100 ml	mls of Stock
0.00	0.00
12.50	2.5
25.00	5.0
37.50	7.5
50.00	10.0

After boiling off NH_3 dilute residue in flask to 100.0 ml
Pipet 10.0 ml or smaller aliquot of ~~sample~~ standard into 25.0 ml volumetric flask; add 10 ml of Color Reagent. - dilute to 25 ml + read
Treat Samples likewise.
Also run Standards and samples without the boiling (direct)
This is a Modified EPA Method

8-28-79

1 2.500 g Urea / 500 ml H_2O
Urea, Baker Reagent Acid ~~Sol~~ 10/6/78

To Page

Witnessed & Understood by me,	Date	Invented by	Date
JMN	8-29-79	Recorded by Margaret Fox	8/28/79

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Project No. 0955-ESO-10
Book No. LAB TITLE W R Grace, Memphis, Tn

Page No. 33

Prep of Urea Audit Sample 8-27-79

Sample #	Weight of whole sample		
1	3.1368 g		
	wt Bottle cap + sample	wt Bottle + cap	wt sample g
2	15.6911	12.1879	3.5032
3	15.2346	12.2688	2.9658
4	15.2606	12.1911	3.0695
5	15.2558	12.1184	3.1374

Each sample was diluted to exactly 100.0 mls with H_2O

Standards

mls of 3 mg/ml Std
0
2.5
5.0
7.5
10.0

5.0 mls of audit sample analyzed – NH_3 boiled off, then diluted to 100 mls

A series of standards and the audit samples will also be analyzed without boiling off NH_3. Direct p-dimethylaminobenzaldehyde colorimetric method (p-dmab)

These will be read at the same time on the colorimeter. And samples calculated ~~bas~~ based on both calibrations for comparison

To Page No. 35

sed & Understood by me,	Date	Invented by	Date
		Recorded by	8/30/79

36

Project No. 0[illegible]-[illegible]80-10

Book No. LAB TITLE W.R. Grace, Memphis, Tn

n Page No. 35

Area Audit Cont'd 8-28-79

Audit Sample NH_3 boiled off

	Sample Volume	Aliquot distilled	the Dilute	Aliquot in 25 ml vol flask	Abs @ 420nm	Equivalent Urea ~~Boiled~~ Distilled	Equivalent Urea Direct std
			= 100.0 mls Solution				
1	100 mls	25.0 ml	5→50,	~~10.0~~ 3.0	.701 high		
				10.0	0.256	2.06	1.803
2				~~10.0~~ 3.0	1.100 high		
			5→50	5.0	0.250	2.01	1.759
boiled ~10 mls 3				~~10.0~~ 3.0	0.972 high		
			5→50	5.0	0.198	1.595	1.376
boiled ~10 mls 4				~~10.0~~ 3.0	0.334	2.648	2.376
5				~~10.0~~ 3.0	0.561	4.556	4.046

If Spectrophotometer is zeroed with distilled urea blank, then the dried urea blank reads 0.004 absorbance.

The audit samples will be calculated 3 ways

1. Direct analysis samples based on Direct standards
2. Boiled samples based on Boiled standards
3. Boiled samples based on Direct standards

To Page No.

essed & Understood by me,	Date	Invented by	Date
			8/30/[illegible]

37 TITLE W R Grace, Memphis, Tn

Project No. 0988-E80-10

Book No. 4B

From Page No. 36 Urea Audit Sample Calculation 8-28-79

① Direct Sample against Direct Standard

Sample ID	Equivalent mg urea (p 35)	Factor	Total mg Urea	mg Urea per gram of sample
1	3.303	$\frac{100\,ml}{4\,ml} \times \frac{50}{5}$	825.8	263.3
2	3.185	$\frac{100}{2} \times \frac{50}{5}$	1592.5	455
3	4.840	$\frac{100}{4} \times \frac{50}{5}$	1210.	408
4	1.553	$\frac{100}{4} \times \frac{50}{5}$	388.2	126.
5	2.516	$\frac{100}{4} \times \frac{50}{5}$	629.	200

② Boiled Sample against Boiled Standards (p 36)

1	2.06 mg	$\frac{100}{25} \times \frac{100}{10} \times \frac{50}{5}$	824	262.7
2	2.01	$\frac{100}{25} \times \frac{100}{5.0} \times \frac{50}{5}$	1608	459
3	1.585	$\frac{100}{25} \times \frac{100}{5.0} \times \frac{50}{5}$	1268	428
4	2.698	$\frac{100}{25} \times \frac{100}{3.0}$	360.	117
5	4.556	$\frac{100}{25} \times \frac{100}{3.0}$	607	193

To Page

Witnessed & Understood by me,	Date	Invented by	Date
		Recorded by Margaret Box	8/25/79

Project No. 0986ESO-10
Book No. LAB TITLE W R Grace, Memphis, Tn

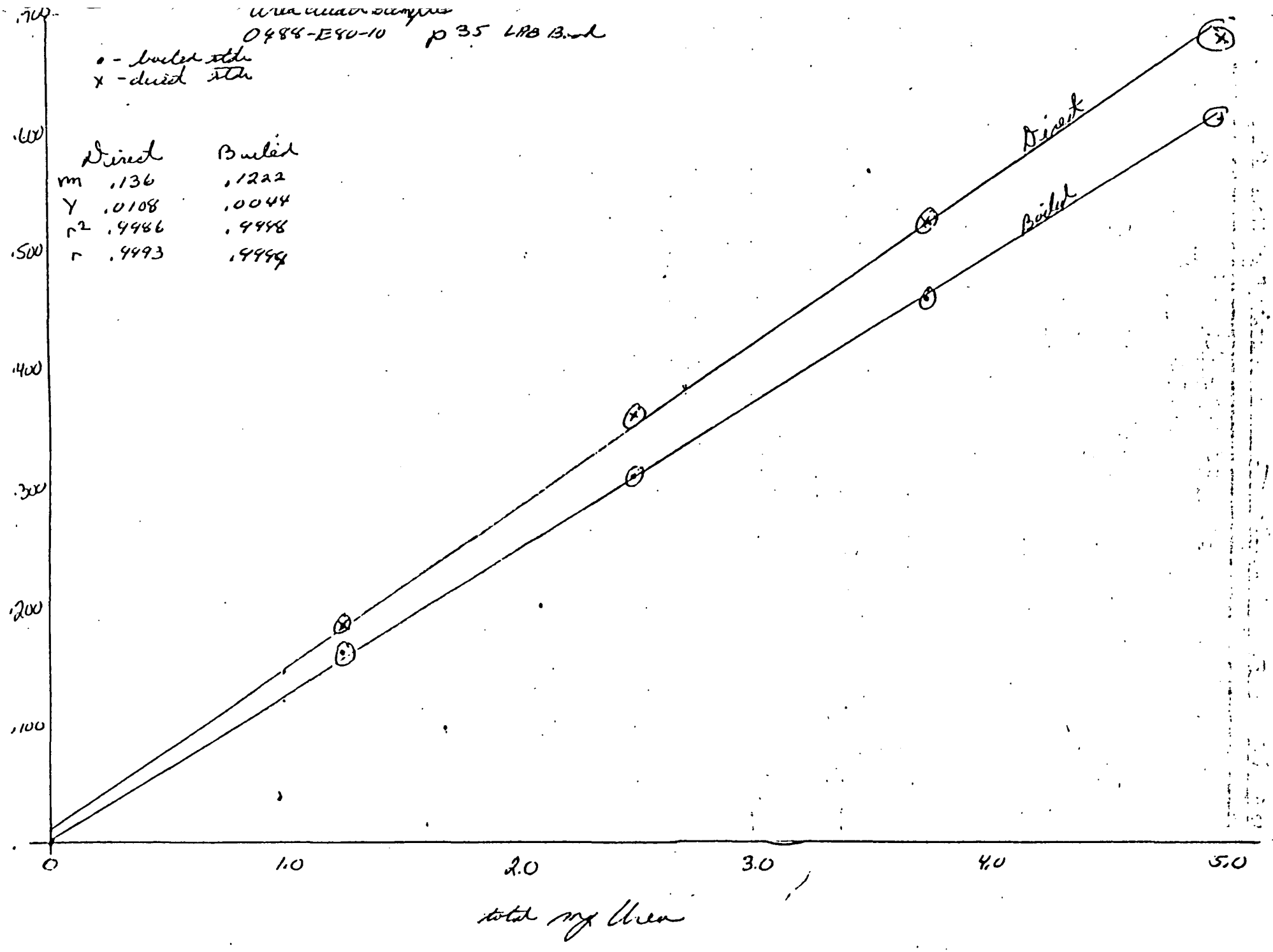
rom Page No. Urea Acetate Sample Calculations cont

(3) Boiled Samples - Direct Standards

Sample ID	Equivalent mg Urea P36	Factors	Total mg Urea	mg Urea per g sample
1	1.803	$\frac{100}{25} \times \frac{100}{10} \times \frac{50}{5}$	721	229.8
2	1.254	$\frac{100}{25} \times \frac{100}{5} \times \frac{50}{5}$	1407	402
3	1.376	$\frac{100}{25} \times \frac{100}{5} \times \frac{50}{5}$	1101	371
4	2.376	$\frac{100}{25} \times \frac{100}{3}$	317	103
5	4.046	$\frac{100}{25} \times \frac{100}{3}$	539	172

To Page No.

Witnessed & Understood by me. | Date | Invented by | Date


0488-E80-10 p 35 LAB Bud
• - boiled sth
x - dried sth
Direct Boiled
m .136 .1222
Y .0108 .0044
r2 .9986 .9998
r .9993 .9999
Direct
Boiled
.700
.600
.500
.400
.300
.200
.100
0
1.0
2.0
3.0
4.0
5.0
total mg Urea

APPENDIX E.2

SULFURIC ACID INTERFERENCE

Project No. 0755-280-40

p43 TITLE W R Grace, Memphis, Tn Book No. LAB

From Page No. — Notes on Urea Analysis p 40-42 8-31-79

The Blank water samples and the Clean up Evaluation samples as well as the samples H^+ (in 1N H_2SO_4) gave absorbances < .000 - the standard Blank 0.000 abs. The W- samples were preserved with 2mL/L H_2SO_4 and the H^+ were 1N H_2SO_4 - The sulfuric acid could be causing a negative interference.

In order to test this, make up ~~standards~~ Blanks with similar concentration of H_2SO_4 and compare the absorbance of these standards, to that of water standards.

Blank ID	Make up	
1	Distilled H_2O	Run through Boiling off NH_3 Prod
2	Millipore H_2O	
3	100 mL of DI H_2O + 0.2 mL H_2SO_4	
4	" " Millipore H_2O + " "	
5	100 mL of 1N H_2SO_4 (DI H_2O)	
6	100 mL of 1N H_2SO_4 (Millipore H_2O)	
~~8~~ 7	10 mL Distilled H_2O	Run direct colorimetric
~~8~~ 8	10 mL Millipore H_2O	

To Page

Witnessed & Understood by me,	Date	Invented by	Date
		Recorded by	

Project No. 0988-E80-10

Book No. LAB TITLE W R Grace, Memphis, Tn

Page No. —

Urea Analysis of Water Impinger 9-4-79

Sample preserved with 2 mL 1½ SO4 / L sample

Standards on p 48

Sample ID	Sample Volume mL	aliquot distilled and diluted to 100 mL	Preliminary Dilution of Distillate	aliquot of distillate or dilution analyzed	Abs @ 420nm	Equivalent mg Urea	FACTORS	ppm Urea	total mg Urea	
wt-2-W-AO	1470	100.0		10.0	.078	0.581	1000/10	58.1	85.41	
wt-2-W-CO	1660	100		10.0	.054	0.401	1000/10	40.1	66.57	
wt-2-W-AI	1525	100		10.0	0.545	4.076	1000/10	407.6	621.6	
wt-2-W-CI	1465	100		10.0	0.198	1.479	1000/10	147.9	216.7	
wt-2-S-I	—	10.0	5→250	10.0	0.441	3.298	1000/10 × 100/10 × 250/5	164,900	—	
wt-2-S-AO	—	10.0	5→250	10.0	0.464	3.470	1000/10 × 100/10 × 250/5	173,500	—	
wt-2-S-CO	—	10.0	5→250	10.0	0.462	3.455	1000/10 × 100/10 × 250/5	172,750	—	
wt-3-W-AO	1710	100.0		10.0	0.045	0.334	1000/10	33.4	57.1	p 97 Sum 622 ave 54.7
wt-3-W-CO	1405	100.0		10.0	0.059	0.439	1000/10	43.9	61.7	
wt-3-W-AI	1580	100.0		10.0	0.425	3.178	1000/10	317.8	502.1	
wt-3-W-CI	1410	100.0		10.0	0.261	1.951	1000/10	195.1	275.1	
wt-3-S-I	—	10.0	5→250	10.0	0.456	3.410	1000/10 × 100/10 × 250/5	170,500	—	
wt-3-S-AO*	—	10.0	5→250	10.0	0.453	3.388	1000/10 × 100/10 × 250/5 × 105/1000	177,570	Repeat Results ~~[illegible]~~ 173,145	p47 ave ~~[illegible]~~ 176,08

* see p 14 - sample diluted by ~ 5%

To Page No. 47

Witnessed & Understood by me, | Date | Invented by | Date

From Page No.— ~~Abs~~ Absorbance Readings of Standard Blanks on p 43 S-3

Use below standards Blank to zero Beckman @ 420nm	Blank ID use 43 for computer	Abs
1	1	.000
	2	.000
	3	-.6
	4	.003
	5	0
	6	0
	7	.001
	8	.000
5	5	.000
~~6~~	6	.008
	1	.047
	2	.048

> -.01

Conclusion:

Make up standards with the same concentration H_2SO_4 as the sample (The difference between a water blank and a 1N H_2SO_4 (10 ml) blk is .048 Abs units @ 420nm).

Standards for W sample should contain 2mL/L H_2SO_4

Standard for H+ sample (Test Test+Test should ~~contain 1N~~ be make up in 1N H_2SO_4

Standards for the acid portion of the Solution Power tests will be made up with 10N (Tests 1+2) 5N H_2SO_4 (Test 3)

Check with Gene Riley - analyzer Scrubber water preserved with 2mL/L H_2SO_4 with the same type field

To Page

Witnessed & Understood by me,	Date	Invented by	Date
		Recorded by Margaret Jop	8/31/79

Project No. 0988-E60-10 p44

Book No. ~~HALPB~~ TITLE W R Grace Memphis, Tn

Page No. Urea Analysis 8-31-79

I will read the absorbance of the samples prepared yesterday (p 40-41) which ~~were~~ were in 1N H_2SO_4 giving the Spec. with a Blank containing 1N H_2SO_4 (#6 p43)

Sample ID	Abs 420nm	Equivalent ~~mg~~ /10ml	ppm	~~total mg~~ Volume, mls	~~totaling~~
H+-AO	.002	<.14	<14	< 380	<5.32
H+-CO	.014 ~~.010~~	.17.0 ~~.102~~	equivalent mg graph p52	430 mls	some aliquot	= 17.0 ppm = 7.31 ~~4.39~~ mg/liter
H+-AI	- 6	<.14	<14	< 420	<5.88
H+-CI	.000	<.14	<14	< 400	<5.60
Dest-H+-AO	- 6	<.14	<14	< 433	<6.06
Dest-H+-CO	.003	<.14	<14	< 370	<5.18
-1-H+-AI	.001	<.14	<14	< 550	<7.7
-1-H+-CI	.000	<.14	<14	< 475	<6.65

The above samples (except Cuer H+-CO) are at the limit of detection of meu - p 52 Graph would be <14.1 ~~ppm~~ Urea

Repeat samples - Cuer H+-CO

Use p52 Graph (std in 1N H_2SO_4) to calculate these samples

To Page No.

Witnessed & Understood by me.	Date	Invented by	Date
			8/31/79

9/8/79

Notes on Problems encountered with the Urea analysis of the acid Samples from the Solution Pouch.

These Samples were collected in 450 mls of 10N H_2SO_4 (Test 1&2) or 450 mls 5N H_2SO_4 (Test 3). They were rinsed with 1N H_2SO_4 and final total volume measured. The Normality of each sample was calculated on p56. Stds of 6N H_2SO_4 were made up for Test 1&2. Stds of 3.7N H_2SO_4 were made up for Test 3. An Equivalent of 100 mls of these Normalities was present in the standards & Samples. Test 1&2 standards & Samples needed ~60 mls 10N NaOH to raised pH to >9.5 for NH_3 distillation. Test 3 standards & samples took 40 mls of 10N H_2SO_4. These samples could not be concentrated to < 100 mls because the NaOH started to precipitate and caused severe "bumping" in the Kjeldahl flasks. The samples and Standards were diluted to 200 mls. 10 ml aliquot was placed in 25 ml volumetric flask for the colorimetric analysis (the sensitivity was ½ that when samples are diluted to 100 mls. 10 mls of →

To Page No. 57

From Page No. 58

"Problem" - cont p 58

when color reagent was added to the 15 sample & std on pp 56 & 57 - all of them had NaOH precipitate out a very large amount - gross turbidity. 2 mls of conc HCl was added to each 25 ml flask and the precipitate dissolved completely for ~~the~~ test 3 and std B. All the others had a very small precipitate in the bottom which would not interfere with the Abs readings. (slightly more HCl should have been added to ~~test~~ these samples before diluting to 250 ml

To Page No.

Witnessed & Understood by me,	Date	Invented by	Date
		Recorded by Margaret Fox	9/8/79

Project No. 0488-E010
Book No. LAB TITLE WRB Mar Memphis, TN

From Page No. —

Comparison of Standard Blanks with Reagent N H_2SO_4 9/8/79

Use Below Standard Blank of set .000 Abs	Blank ID	Abs
6N	" 6N	.000
	" 5.8	-.5
	" 6.2	0
	" 3.7	-.7
6.2	6.2	.000
	6N	.027

To Page

Witnessed & Understood by me,	Date	Invented by	Date

APPENDIX F

THRESHOLD MINIMUM DETECTABLE LIMIT FOR THE PROPOSED EPA UREA ANALYTICAL METHOD

from Page No. EPA Contract # 68-02-2520 Assignment # 11 3/10/80
Technical Direction 2/13/80 Threshold Evaluation
Matter - Determination of Particulate, and Urea Emission from Urea Plants Jan 10, 1980

Prepare 1.0000 g/l Urea Working solution = 1000 mg/l = 1 mg/ml

Set I		mg/100 ml	ml WS in 100	Abs 1cm	Abs 5cm
1	50 mg urea/l	5	5	~~.090~~ .087	.368
2	100	10	10	.157	.678
3	150	15	15	.250	.860
4	200	20	20	.332	.984
5	250	25	25	.415	1.044
0	Blank			.000	.000

Set II - Dilute 1 mg/ml WS 10 ml → 100 ⇒ 0.100 mg/ml WS 2

		mg/100 ml	ml WS in 100	Abs 1cm	Abs 5cm
2-1	1 mg urea/l	0.10	1	(-.009) -.007	< 0 (~~-.0~~)
2-2	2	0.20	2	ok .000	.003
2-3	5	0.50	5	(.003) .003	.013
2-4	7	0.70	7	.010	.048 ~~.055~~
2-5	10	1.00	10	(.013) .015	.067
2-6	20	2.00	20	.032 .033	.132
2-7	30	3.00	30	.051 ~~.055~~	.273

Use 20.0 ml Sample + 20 ml Urea color Reagent → 50.0 ml

1-0 b .053

To Page No. 77

Witnessed & Understood by me,	Date	Invented by	Date
		Recorded by Margaret McFee	3/11/80

From Page No. 76

Linear Regression * 3/10/80

	(A) Set I 1cm Cell	(B) Set II 1cm cell	(C) Set I 5cm	(D) Set II 5cm
r	.9996	0.9914	0.9685	0.9946
m	.0016589	0.0018478	0.0041771	0.0075~~408~~739
y-int	-.0005238	-.0041977	0.1235	-0.0~~099454~~106386

Plot (A) x	y	Plot (B) x	y	Plot (C) x	y	Plot (D) x	y
75	.124	6	.0069	75	.437	6	.0~~353~~048
175	.290	15	.0235	175	0.854	15	0.1032

ppm Set II based on Graph Set I 1cm

		actual mg/l
1	-3.90 mg/l Urea	1.0
2	0.316	2.0
3	2.12	5.0
4	6.34	7.0
5	9.36	10.0
6	20.21	20.0
7	31.06	30.0

* The linear Regression were calculated using x = ppm value
y = Absorbance value
y use the blank point x = 0 mg/l
y = 0.000 Abs.

Conclusions 7 ppm Urea appears to be the limit of detection for this method. The 5cm cell (see Graph D) does not ~~extend~~ increase the sensitivity of this method.

To Page No.

Witnessed & Understood by me, | Date | Invented by | Date 2/11/80

APPENDIX G

UREA SAMPLING TRAIN COLLECTION EFFICIENCY

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

April 10, 1980

Mr. Will Wade
TRC Environmental Consultants, Inc.
125 Silas Deane Highway
Wethersfield, Connecticut 06109

Reference: EPA Contract No. 68-02-2820, Assignment No. 20, Union Oil Company, Brea, California, EMB Report No. 80-NHF-15

Dear Will:

This letter is to document and clarify the scope of work proposed under the above referenced work assignment.

Test Program Sampling and Analytical Procedures

Three individual urea-ammonia particulate runs shall be performed at the prill tower Northeast stack. The test runs shall be conducted at the outlet location while the tower is producing fertilizer grade prills. The three runs shall each cover approximately 144 minutes over 48 traverse points.

The train configuration shall consist of a glass-lined probe connected by a flexible Teflon line to six(6) impingers. The first two impingers are to be prefilled with deionized, distilled water (100 mls each). The next two are to be prefilled with 1N H_2SO_4 (100 mls each). The fifth impinger shall remain empty while the sixth shall be prefilled with 200 grams of indicating silica gel.

The first, third, fifth, and sixth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with an 1/2 inch glass tube extended to within 1/2 inch of the impinger's bottom.

The second and fourth impingers are of the regular design for the Greenburg-Smith units including tips with orifice plates located within 1/2 inch of the bottom. No filter is required.

The probe shall be heated to the temperature range of the stack plus 10°F. The probe temperature shall be measured and recorded for each point. However, if you do not have this capability you may record the variable transformer setting and submit calibration curves utilizing the procedures outlined in APTD-0576. Data measurements shall be required for each traverse point. In addition the train operator shall maintain a daily log detailing problems, delays, elapsed sampling times, and associated comments.

Sample cleanup and recovery procedures include the following:

(1) The probe, flexible Teflon line, and their connecting glassware shall be rinsed with deionized, distilled water into one container. The probe shall be brushed and rinsed.

(2) The first impinger's contents shall be placed in a second container. The impinger and its U-tube shall be rinsed with deionized, distilled water into the same container.

(3) The second impinger's contents shall be placed in a third container. The impinger and its U-tube shall be rinsed with deionized, distilled water into the same container.

(4) The third, fourth and fifth impingers and their connecting glassware shall be rinsed with a 1N H_2SO_4 solution and placed in a fourth container.

Brush and rinse the parts in the above prescribed manner at least three times or until no visible particles remain.

The prill tower emission samples shall be analyzed as follows:

1. Analyze each individual water portion for urea content by the colorimetric (p-dimethylaminobenzaldehyde) procedure - add buffer compound, boil off ammonia and analyze for urea.

2. Analyze the combined water portion (probe, first and second impinger water) for ammonia content by the Specific Ion Electrode method.

3. Analyze the 1N H_2SO_4 portion for urea content by the above colorimetric procedure - caution should be used as an interference problem (turbidity) is expected. These values are not to be combined with the urea values from the water portions when calculating the emission rates.

4. Analyze the 1N H_2SO_4 portion for ammonia content by specific ion electrode.

Contractor shall analyze the three outlet samples for urea by the colorimetric procedure within 20 days after collection.

Contractor shall analyze all emission samples for ammonia by Specific Ion Electrode within 20 days after collection.

Scrubbing liquor aliquots shall be collected approximately every 30 minutes during the test periods. Aliquots shall be collected at an existing valve located in the low pressure scrubber solution recirculating system (see Figure 1).

For each aliquot sample, the temperature shall be measured following its collection time and the pH shall be measured as soon as the sample reaches room temperature (70°F). Afterwards, the aliquots are to be combined to form one composite sample per run.

TRC – Environmental Consultants, Inc.

Report of Chemical Analysis of Non-Routine Samples

Client: EPA - Union Oil
Contract No: 0988-E60-91
Reviewed by:
Report to: W. Wade

Laboratory No: 185-80-(5)
Date Received: 5-1-80
Date Reported: 5-23-80

Type Sample: Filter ____ Fuel Oil ____ Sediment ____ Impinger ✓ Other Scrubber Water

Sample Number	Location	Analysis No. 1 Urea	Analysis No. 2 Ammonia Specific Ion	Analysis No. 3 mg/l Solids	Analysis No. 4	Analysis No. 5	Analysis No. 6
1-PL	Prill Power	4.50 mg	5.43 mg				filtered out orangish particle
1-1	"	44.6 mg	72.6 mg				"
1-2	"	28.8 mg	26.9 mg				
1-3,4,5	"	nd <1.64 mg *	67.5 mg				
S-1-comp	Scrubber Water	24,300 mg/l	—	15.5 mg/l			
2-PL	Prill Power	4.83 mg	2.83 mg				
2-1	"	31.8 mg	50.1 mg				
2-2	"	13.5 mg	40.1 mg				
2-3,4,5	"	nd <1.58 mg *	102 mg				
S-2-comp	Scrubber Water	22,500 mg/l	—	5.9 mg/l			

*- Do not combine this urea value from the acid impingers with the water urea results when calculating the emission results

Analyzed by: MMF / [illegible]

Form [redacted] 0012 [redacted]

TPC [redacted] Environmental Consultants, Inc. [redacted]

Report of Chemical Analysis of Non-Routine Samples

Client: EPA-Union Oil

Contract No: 0988-ESO-91

Reviewed by:

Report to: W. Wade

Laboratory No: 185-80 (5)

Date Received: 5-1-80

Date Reported: 5-28-80

Type Sample: Filter ____ Fuel Oil ____ Sediment ____ Impinger ✓ Other Scrubber Waters.

Sample Number	Location	Analysis No. 1 Urea	Analysis No. 2 Ammonia specific Ion	Analysis No. 3 Solids	Analysis No. 4	Analysis No. 5	Analysis No. 6
3-PL	Prill Tower	5.58 mg	3.1 mg				
3-1	"	41.1 mg	110. mg				
3-2	"	15.3 mg	63.3 mg *				
3-3,4,5	"	nd < 1.49 mg	199 mg				
5-3-comp	Scrubber Water	24,200 mg/l	—	64.4 mg/l			
4-PL-12	Prill Cooler Inlet	5,357 mg	21.7 mg				filtered
4-3,4,5	"	n.d. < 1.71 mg	nd < 7.6 mg *				
5-PL-12	"	3,780 mg	225 mg				filtered
5-3,4,5	"	nd < 1.53 mg	9.38 mg *				
							filtered ↓
6-PL12	"	4517	23.9 mg				
6-3,4,5	"	nd < 1.89 mg	125 mg *				

* Do not combine this urea value from the acid impinger with the water urea values when calculating the emission results

Analyzed by: MMP / DWA

Form CL-0012, Rev.

TRC – Environmental Consultants, Inc.

Report of Chemical Analysis of Non-Routine Samples

Client: EPA - Union Oil

Contract No: 0988-E80-91

Reviewed by:

Report to: W. Wade

Laboratory No: 185-80(5)

Date Received: 5-1-80

Date Reported: 5-[illegible]-80

Type Sample: Filter ____ Fuel Oil ____ Sediment ____ Impinger ____ Other Blanks

Sample Number	Location	Analysis No. 1 Urea	Analysis No. 2 Ammonia Specific Ion	Analysis No. 3 Solids	Analysis No. 4	Analysis No. 5	Analysis No. 6
B-PL12	Scrubber Outlet	nd < 1.98 mg	nd < 0.38				
B-3,4,5		nd < 1.82 mg	nd < 4.04				
Field Blank H_2O		nd < 2.6 mg/l ppm	nd < 1.0 mg/l ppm				
Field Blank H_2SO_4		< 9.0 mg/l					

Analyzed by: [illegible]

Project No. 0988-E80-97
Book No. RC-188 TITLE ~~Rockhold Chemical~~ Union Oil

Page No. ____

5/10/80

Sample volumes

ID	volume ml	type	filter #	
1-PL	765	imp H_2O	5015	(rusty ~~orange~~ particles)
1-1	~~50~~ 300.	↓	5016	"
1-2	215	↓		
1-3,4,5	365	imp acid		
S-1 comp.	470	scrubber	5017	
2-PL	690	imp H_2O		
2-1	208	↓		
2-2	175	↓		
2-3,4,5	350	imp acid		
S-2-comp	440	scrubber	5018	
3-PL	620	imp H_2O		
3-1	220	↓		
3-2	185	↓		
3-3,4,5	332	imp acid		
S-3-comp	455	scrubber	5019	
4-PL12	1,090	Water imp	5020	(yellowish filtrate)
4-3,4,5	380	imp acid		
5-PL12	945	Water imp	5021	
5-3,4,5	340	imp acid		
6-PL12	1,040	Water imp	5022	
6-3,4,5	420	imp acid		
B-PL12	380	H_2O	cleanup scrubber outlet	
B-3,4,5	202	acid	↓	↓

To Page No. ____

Witnessed & Understood by me,	Date	Invented by	Date
		Recorded by Margaret M. Fry	5/14/80

TITLE Reichhold Chemical

Project No. 0488-080-70
Book No. RC-LAB

From Page No.

Prepare Urea Standards 5/10/80

Stock 5,000 g/l Urea (4-29-80) DWA

ml stock in 250	total mg Urea in 250	total mg in 100	mg in 10 ml	Abs	(corr) Abs
0			0	.000	
2.0			.4	.034	
5.0			1.0	.091	
10.0			2.0	.169	(.165)
20.0			4.0	.334	(~~.344~~ .332)
25.0			5.0	~~.461~~ .453	

Linear Regression

m = 0.088
y = -0.002
r = 0.9983

Plot

x	y
1.5	.130
3.5	.306

Limit of detection for 0.01 Abs = <0.13

y = .181

2nd slope m
2nd Corr r
2nd Intcp y

To Page No.

Witnessed & Understood by me,	Date	Invented by	Date
S Chu 5/22/80		Recorded by Margaret M. Fox	5/19/80

Project No. 0988-000-91
Book No. EC-LAB TITLE Union Oil

Page No. ___

Urea analysis 5/10/80

Sample ID	Volume sample	Aliquot distilled & residue/more	dilution	Aliquot Analyzed	Abs	equivalent mg Urea	FACTOR	PPM Urea mg/l	Total mg Urea
1-PL	765	500 mls	—	10	.024	0.294	$\frac{1}{10}\times\frac{100}{500}\times 1000$	5.88	4.50 ✓
1-1	300	200 mls	—	10	.260	2.97	$\frac{1}{10}\times\frac{100}{200}\times 1000$	148.5	44.6
1-2	215	150 mls	—	10	.175	2.01	$\frac{1}{10}\times\frac{100}{150}\times 1000$	134	28.8
S-1	—	200 mls	5 → 200	~~10~~ → 2.0	.212	2.43	$\frac{1}{2}\times\frac{100}{200}\times\frac{200}{5}\times 1000$	24,300	—
2-PL	690	500	—	10.0	.029	0.35	$\frac{1}{10}\times\frac{100}{500}\times 1000$	7.0	4.83
2-1	208	150	—	10.0	.200	2.29	$\frac{1}{10}\times\frac{100}{150}\times 1000$	152.7	31.8 ✓
2-2	175	100	—	10.0	.066	0.771	$\frac{1}{10}\times\frac{100}{100}\times 1000$	77.1	13.5 5/12/80
S-2-comp	—	200	5 → 200	2.0	.196	2.25	$\frac{1}{2}\times\frac{100}{200}\times\frac{200}{5}\times 1000$	22,500	—
3-PL	620	~~500~~ 400	—	10.0	.030	0.36	$\frac{1}{10}\times\frac{100}{400}\times 1000$	9.0	5.58 ✓
3-1	220	100	—	10.0	.163	1.87	$\frac{1}{10}\times\frac{100}{100}\times 1000$	187	41.1
3-2	185	100	—	10.0	.071	0.828	$\frac{1}{10}\times\frac{100}{100}\times 1000$	82.8	15.3
S-3 comp	—	200	5 → 200	2.0	.211	2.42	$\frac{1}{2}\times\frac{100}{200}\times\frac{200}{5}\times 1000$	24,200	—
4-PL12	1090	700	5 → 200	2.0	~~0.14~~ 0.150	1.72	$\frac{1}{2}\times\frac{100}{700}\times\frac{200}{5}\times 1000$	4,914	5,357
5-PL12	945	700	5 → 200	2.0	0.122	1.40	$\frac{1}{2}\times\frac{100}{700}\times\frac{200}{5}\times 1000$	4,000	3,780 ✓
6-PL12	1040	700	5 → 200	2.0	0.132	1.52	$\frac{1}{2}\times\frac{100}{700}\times\frac{200}{5}\times 1000$	4,343	4,517

See Note p 38

To Page No. ___

Witnessed & Understood by me, Clin 5/22/80 | Date | Invented by | Date

Recorded by Margaret Dp | 5/19/80

TITLE Union Oil

Project No. 0988-E&O-91
Book No. RC-LAB

From Page No. ___

Urea Analysis 5/12/80

Sample ID	Volume Sample	Aliquot distilled + residue to 100 mls	dilution	Aliquot Analyzed	Abs	equivalent mg Urea	FACTORS	ppm Urea mg/l	Total mg Urea
B-1,2,4,P,	380	250	—	10.0	.006	nd <0.13	$\frac{1}{10}\times\frac{100}{250}\times1000$	<5.2	<1.98
Blank Field	—	500	—	10.0	.006	nd <0.13	$\frac{1}{10}\times\frac{100}{500}\times1000$	<2.6	—
Blank TIC	—	500	—	10.0	.000	nd <0.13	$\frac{1}{10}\times\frac{100}{500}\times1000$	<2.6	—
Below Samples are in 1.0 N H_2SO_4 (std p 39) 5/12/80									
1-3,4,5	365	200 mls	none	10.0	.001	nd <.09	$\frac{1}{10}\times\frac{100}{200}\times1000$	<4.5	<1.64
2-3,4,5	350	200			.000	nd <.09		<4.5	<1.58
3-3,4,5	332	200			.003	nd <.09		<4.5	<1.49
4-3,4,5	380	200 ml			.006	nd <.09		<4.5	<1.71
5-3,4,5	340	200			.003	nd <.09		<4.5	<1.53
6-3,4,5	420	200 mls			.000	nd <.09		<4.5	<1.89
Field air Blank	—	100			.000	nd <.09	$\frac{1}{10}\times\frac{100}{100}\times1000$	<9.0	<
B-3,4,5	202	100			.000	nd <.09		<9.0	<1.82

To Page No.

Witnessed & Understood by me, S. Chn 5/22/80

Date

Invented by

Date

Recorded by Margaret M. Fry

5/19/80

APPENDIX H

SCOPE OF WORK

Includes:

Work Assignments
Technical Directives

82488

WORK ASSIGNMENT ENVIRONMENTAL PROTECTION AGENCY Research Triangle Park, N.C. 27711	EPA CONTRACT NO. 68-02-2820 CONTRACTOR TRC of New England ASSIGNMENT NO. 11 ASSIGNMENT CHANGE NO.
TITLE Conduct Emission Test Program at an Urea Manufacturing Plant	DATE 5 DEC 1978

DESCRIPTION

The Contractor shall perform an emission test program in accordance with the basic contract scope of work for the Emission Measurement Branch, and as set forth in the attached "Source Sampling and Analysis Schedule" at the following site:

Company: Agrico Chemical
Location: Blytheville, Ark.
Industry: Ammonium Fertilizer
Project No.: 79-NHF-13

The Emission Measurement Branch's Technical Manager is Clyde E. Riley. Mail Drop 13, EMB, ESED, OAQPS, Research Triangle Park, North Carolina 27711.

Upon notification of approval of the proposed source test report, the Contractor shall provide 25 copies of the final report with appendices.

ESTIMATE OF	GOVERNMENT ESTIMATE	CONTRACTOR ESTIMATE
LABOR HOURS	200	200
DURATION OF WORK	3 months	3 months
COMPLETION DATE	March 31, 1979	March 31, 1979

REQUESTER'S SIGNATURE	ORG CODE	TELEPHONE	DATE
Clyde E. Riley C. E. Riley 11-30-78	ESED/EMB	(919) 541-5243	11/30/78

APPROVALS (as applicable)	SIGNATURE	DATE
BRANCH CHIEF	R. E. Mularkey for George Wilson	11/30/78
DIVISION CHIEF	Dale R. Patterson	12-5-78
PROJECT MANAGER	Thomas M. Bibb	12/4/78
CONTRACTING OFFICER	C. Hicks	12-5-78

CONTRACTOR'S REPRESENTATIVE ACKNOWLEDGMENT

SIGNATURE

08-02-2820

SOURCE SAMPLING AND ANALYSIS SCHEDULE

See Figure 1

Company: Agrico Chemical

Company Location: Blytheville, Ark.

Industry: Ammonium Fertilizer

Process: Urea Granulator

Control Equipment: Scrubber

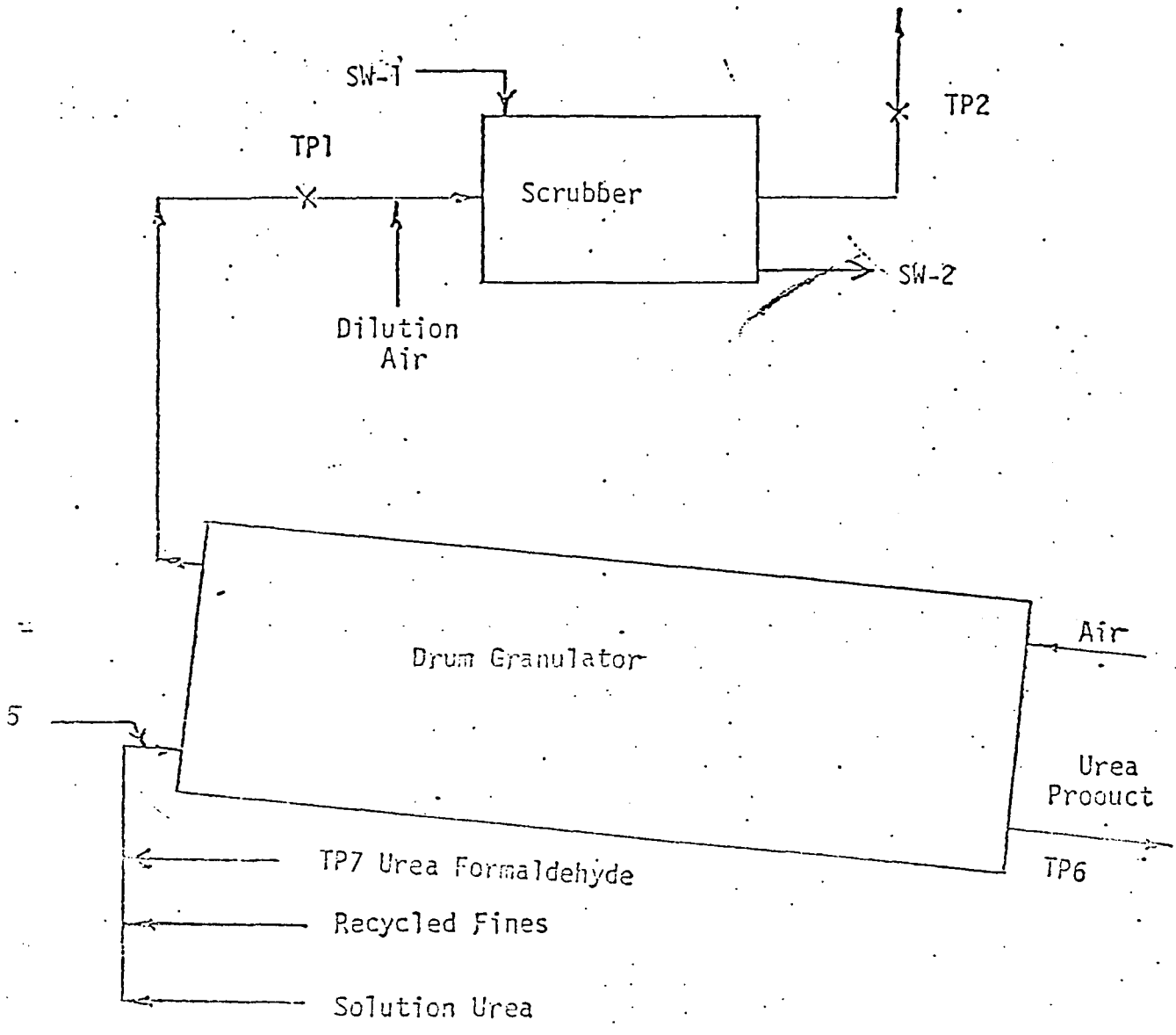
Sampling Point Figure	Total No. of Samples	Sample Type	Sampling Method	Sample Collected By	Minimum Sampling Time	Minimum Gas Volume Sampled ft^3	Initial Analysis Type	Initial Analysis Method	Initial Analysis By	Final Analysis Type	Final Analysis Method	
P2	6	Urea Particulate	Modified EPA-5	CTR	60	30	Urea Mass	Kjeldahl	CTR.	Ammonia	(EPA) Nessler	CTR
Aliquots shall be collected from each of the above 6 samples							Urea Mass	Kjeldahl	Agrico			
Sample analysis shall be conducted within 24 hours of collection on each of the H_2O samples.												
After completion of analysis remaining samples shall be split into 2 equal portions and treated with a stabilizer.												
One portion shall be treated with saturated mercuric chloride (approximately 2 ml per liter of water)												
Second portion shall be treated with concentrated sulfuric acid (approximately 2 ml per liter of water)												
These solutions shall be returned to the TRC lab and allowed to stand at room temperature for a period of 20 days; however they shall be analyzed by the Kjeldahl urea method once every two days for urea content during this period.												
SW-1	6	Scrubber Solution In	Composite	EPA	N. A.	N. A.	Percent Solids	Filtration	CTR	Urea	Kjeldahl	CTR
										NH_3	Nessler	CTR
SW-2	6	Scrubber Solution Out	Composite	EPA	N. A.	N. A.	Percent Solids	Filtration	CTR	Urea	Kjeldahl	CTR
										NH_3	Nessler	CTR

REMARKS:

1. Sampling shall be performed with ± 10% isokinetic conditions.
2. Methods are EPA unless indicated otherwise.
3. Impingers and analysis of impinger catch will be per the Federal Register, Volume 36, No. 159, Part II, Tuesday, Aug. 17, 1971, unless specifically changed by the Project Officer.
4. Sampling time and gas volumes are for each sample.

Simultaneous Sampling Required
CTR=Contractor, EPA=Environmental Protection Agency

Figure 1
Agrico Co./The Williams Co., Blytheville, Arkansas



A. Urea Method Development Instructions

1. Contractor shall determine stability conditions for the following six urea solution concentrations. TRC shall use the Kjeldahl urea method to analyze for urea content and the Nessler method to determine the ammonia content.

   a. 40 mg of urea per liter of water

   b. 100 mg of urea per liter of water

   c. 40 mg of urea per liter of water with 2 ml of saturated mercuric chloride solution added

   d. 100 mg of urea per liter of water with 5 ml of saturated mercuric chloride solution added

   e. 40 mg of urea per liter of water with 2 ml of concentrated sulfuric acid added

   f. 100 mg of urea per liter of water with 5 ml of concentrated sulfuric acid added.

   These solutions shall be allowed to stand at room temperature for a period of 20 days; however, they shall be analyzed once every 2 days for urea and ammonia content. Questions regarding these instructions or the urea and ammonia analysis procedures shall be directed to Mr. Gary McAlister at 919-541-5276.

2. Contractor shall prepare two duplicate sets of "dry" urea audit samples. Each set shall contain 12 individual urea samples. Both sets of samples shall be forwarded to the Agrico Chemical plant in Blytheville, Arkansas, by TRC personnel. One set of samples shall be analyzed by Agrico personnel and the second set shall be analyzed by TRC personnel.

3. Agrico audit sample analysis shall be performed according to methods and procedures employed while analyzing the urea samples generated during the October 9, 1978, EPA test program.

4. TRC audit analysis shall be performed using the Kjeldahl urea method as directed by Mr. Gary McAlister, EPA.

5. Contractor shall specify procedures directing Agrico personnel to dilute the 12 audit samples with solutions of water and/or 1N H_2SO_4. Audit sample analyses shall be conducted within 12 hours after dilution. The 12 audit samples shall be prepared and diluted as follows:

Dilute With 400 mls H_2O		Dilute with 250 mls 1N H_2SO_4	
No. 1	100 mg urea	No. 7	2 mg urea
No. 2	300 mg urea	No. 8	5 mg urea
No. 3	600 mg urea	No. 9	10 mg urea
No. 4	5 mg urea	No.10	5 mg urea
No. 5	10 mg urea	No.11	4 mg urea
No. 6	40 mg urea	No.12	30 mg urea

B. Agrico Test Program

1. Contractor shall collect six urea particulate samples from one of the operating granulator outlet stacks. Samples shall be collected using isokinetic sampling conditions for a period of approximately 1 hour. The collection train shall consist of a probe heated to stack temperature, a flexible teflon line, and five impingers. The first three impingers shall each be prefilled with 100 mls

Dist. H_2O, the fourth shall remain empty, and the fifth shall contain approximately 200 gms of silica gel. The second and third shall be of the Greenburg-Smith design with standard tips. The first, fourth, and fifth shall be modified with a 1/2" tube.

2. Cleanup shall consist of measuring the solution volumes and rinsing the probe, flex line, and impinger several times (3) with Dist. H_2O. Afterwards the water samples shall be filtered through a preweighed fiber glass filter using a Buchner funnel and vacuum pump.

3. Analysis shall consist of weighing the liquid samples initially. Afterward two equal aliquots shall be withdrawn. One aliquot shall be analyzed for urea and ammonia by Agrico personnel using the Kjeldahl urea method. The second aliquot shall be analyzed for urea and ammonia by TRC personnel using the Kjeldahl method as directed by EPA. Sample analysis shall be conducted within 24 hours of collection of all samples.

   After the two analysis aliquots have been withdrawn the remaining sample volumes shall be split into two equal portions and treated with a stabilizer solution. One portion shall be combined with a saturated mercuric chloride solution (approximately 2 mls per liter of water). The second portion shall be combined with concentrated sulfuric acid (approximately 2 mls per liter of water).

4. These solutions shall be returned to the TRC laboratory and allowed to stand at room temperature for a period of 20 days; however, they shall be analyzed by the Kjeldahl urea method once every 2 days during this period for urea and ammonia content.

5. The preweighed glass fiber filters used to filter the water solutions shall be returned to the TRC laboratory, dried and weighed for undissolved solids.

6. Contractor shall separate and report all Research and Development data in a separate EPA proposed draft report. These method and evaluation data shall not be included in the Agrico NSPS report. Contractor shall submit 3 copies of the proposed R&D final report directly to Mr. J. E. McCarley, EMB, ESED, Mail Drop 13, Research Triangle Park, N. C. 27711. The separate R&D report shall be entitled "Development of Analytical Procedures for the Determination of Urea from Urea Manufacturing Facilities" and listed under Project No. 79-NHF-13.

EMISSION MEASUREMENT BRANCH

TECHNICAL DIRECTIVE NO. 1

Project Number 79-NHF-13 Date February 16, 1979

Contractor TRC of New England

Contract Number 68-02-2820 Work Assignment Number 11

Technical Manager Clyde E. Riley

Verbal Directions Given To Will Wade

Directive:

1. The Contractor shall perform formaldehyde analysis on each of the six urea particulate samples.

Clyde E. Riley C. E. Riley
Technical Manager, EMB

Section Chief, EMB

EMISSION MEASUREMENT BRANCH

TECHNICAL DIRECTIVE NO. 2

Project Number 79-NHF-13 Date March 21, 1979

Contractor TRC of New England

Contract Number 68-02-2820 Work Assignment Number 11

Technical Manager Clyde E. Riley

Verbal Directions Given To Mr. Will Wade

Directive:

See attached pages.

Clyde E. Riley
Technical Manager, EMB

Section Chief, EMB

Contractor shall perform the following evaluation analyses:

1. Prepare an urea standard solution containing 2mg urea/ml H_2O

   Weigh 0.2000g of urea into a 100 ml volumeteric flask and dilute to 100 ml with deionized, distilled H_2O.

2. Prepare an ammonia standard solution containing 20 mg NH_3/ml H_2O

   Weigh 31.4100g of NH_4Cl into a 500 ml volumeteric flask and dilute to 500 ml with deionized, distilled H_2O.

3. Prepare nine samples from the above standards as follows:

Sample Nos.	ml of Urea Std.	ml of NH_3 Std.	Total Volume ml
1	5	0	100
2	5	0	200
3	15	0	200
4	10	0	100
5	10	1	200
6	10	5	200
7	5	5	100
8	5	25	100
9	5	50	100

   Note: Samples must be analyzed within 24 hours after being prepared.

4. Analyze the nine samples using the colorimeteric (p-aminobenzaldehyde) procedures. Use samples 1,2,3, and 4 to prepare a standard curve.

5. Calculate the measured values for the remaining samples 5 through 9.

6. Data shall be presented in mg urea/ml of solution along with the standard curve.

If additional information is required please contact Mr. Gary McAlister at 919/541-2237. MD-19

cc: Gary McAlister
File: 79-NHF-13

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

February 13, 1980

Mr. Will Wade
TRC of New England
125 Silas Deane Highway
Wethersfield, Connecticut 06109

Reference: EPA Contract No. 68-02-2820, Assignment No. 11, Agrico Chemical, Blytheville, Arkansas, EMB Report No. 79-NHF-13

Dear Will:

This correspondence is to document the enclosed Technical Directive instructions for conducting an evaluation of slope linearity for standard urea curves.

It has come to our attention that the standard curve slope may change with low-urea concentrations. In order to verify this conjecture Mr. Gary McAlister has requested that curves for two sets of standard samples be compared. The first set of standard samples will range from 50 mg urea/liter to 250 mg urea/liter. The second set will range from 1 mg urea/liter to 30 mg urea/liter. Standard solutions containing the following urea concentrations will be used to establish the two curves.

Set No. 1	Set No. 2
1. 50 mg urea/liter	1. 1 mg urea/liter
2. 100 mg urea/liter	2. 2 mg urea/liter
3. 150 mg urea/liter	3. 5 mg urea/liter
4. 200 mg urea/liter	4. 7 mg urea/liter
5. 250 mg urea/liter	5. 10 mg urea/liter
	6. 20 mg urea/liter
	7. 30 mg urea/liter

TRC shall prepare and analyze the standard solutions as follows.

Samples containing urea and deionized distilled water shall be made up in 100 ml volumeteric flasks.

Samples shall be analyzed by the P-dimethylaminobenzaldehyde colorimeteric procedure. Do not boil off the samples as there should be no impurities present to interfere with the analyses.

Establish calibration curve No. 1 using urea results obtained from Set No. 1 samples.

Determine urea concentrations from calibration curve No. 1 using measured values obtained from Set No. 2 samples.

Establish calibration curve No. 2 using urea results obtained from Set No. 2 samples.

Compare the slope of the No. 1 curve to the slope of the No. 2 curve.

Please report your conclusions and recommendations along with a summary of the data to me by March 14, 1980. These data will be used to establish guidelines for the upcoming prill tower test in St. Helens, Oregon.

If you have any questions regarding these instructions or require additional information, please do not hesitate to contact me.

Sincerely yours,

Clyde E. Riley

Clyde E. Riley
Field Testing Section
Emission Measurement Branch

Enclosure

cc: Gary McAlister
Marge Fox, TRC

EMISSION MEASUREMENT BRANCH

TECHNICAL DIRECTIVE NO. 4

Project Number 79-NHF-13 Date Feb. 12, 1980

Contractor TRC of New England

Contract Number 68-02-2820 Work Assignment Number 11

Technical Manager Clyde E. Riley

Verbal Directions Given To Mr. Reed Cass

Directive:

Contractor shall determine slope linearity for standard urea curves using the following sets of samples.

Set No. 1

1. 50 mg urea/liter
2. 100 mg urea/liter
3. 150 mg urea/liter
4. 200 mg urea/liter
5. 250 mg urea/liter

Set No. 2

1. 1 mg urea/liter
2. 2 mg urea/liter
3. 5 mg urea/liter
4. 7 mg urea/liter
5. 10 mg urea/liter
6. 20 mg urea/liter
7. 30 mg urea/liter

Contractor shall prepare and analyze samples per instructions presented in February 12, 1980 correspondence to Mr. Will Wade.

Clyde E. Riley 2-12-80
Technical Manager, EMB

Section Chief, EMB