SOURCE EVALUATION SOCIETY
P.O. Box 12124
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NEWSLETTER

Vol. XIII, No. 1 February 1988

CONTENTS

TECHNICAL ARTICLES

1. Summary of EPA Test Methods as of March 1, 1988.

2. Foston Curtis, "Analysis of Method 6 Samples in the Presence of Ammonia," Emission Measurement Branch, TSD, OAQPS, EPA, February 1988.

SOCIETY NEWS ITEMS

1. SES Accreditation/Certification Program. Proposed amendments to the SES Constitution and Bylaws have been sent to all members. If you have not received a copy, please inform your president, Charles F. Duncan.

2. This is a reminder to all SES members. One of the goals of this Society is to develop and disseminate technical information in order to provide a continuing education to source samplers, the industries they serve, and mankind in general. If we are to accomplish this goal, WE NEED to do OUR PART. So, please CONTRIBUTE technical articles to the SES Newsletter.

3. SES Membership List. Late renewals and new members are listed in this issue. Membership now numbers 245.

TECHNICAL NEWS ITEMS

1. Six-Month Outlook for Method and Revision Proposals. If you are interested in helping to formulate new, revised, or alternative test methods, be on the lookout for the following probable proposals in the Federal Register over the next six months.

a. Test Methods/Test Methods and Procedures Sections of Part 61. Corrections.

b. Method 21 Revisions.

c. Methods 15/16 Revisions.

d. PM_{10} Test Method.

e. Method 108B, C, and D Alternative Methods for Arsenic.

f. Method 9B Transmissometer Method.

2. Test Method Proposals and Promulgations.

a. Revised Method 19. Promulgated 12/16/87 (52 FR 47826). Method 19A has been incorporated into Method 19 and promulgated with the Industrial-Commercial-Institutional Steam Generating Units standards.

b. Method 16A Revisions/Method 16B Addition. Correction Notice 2/2/88 (53 FR 2914).

c. Revised Method 25. Promulgated 2/12/88 (53 FR 4140). The revised Method 25 has been published in the Federal Register.

d. Test Methods and Procedures in 40 CFR Part 60. Proposed 2/19/88 (53 FR 5082). Test methods and procedures necessary to determine compliance with the applicable standards or related monitoring requirements have been consolidated into one paragraph.

e. Methods 5G, 5H, 28, and 28A. Promulgated 2/26/88 (53 FR 5860). These test methods are used for testing the performance of residential wood heaters and have been promulgated with the standards. Only accredited laboratories are allowed to test these wood heaters.

3. NSPS and NESHAP Proposals and Promulgations.

a. Industrial-Commercial-Institutional Steam Generating Units. Promulgated 12/16/87 (52 FR 47826). Standards of performance under Subpart Db of 40 CFR Part 60 limiting emissions of sulfur dioxide from coal- and oil-fired industrial-commercial-institutional steam generating units and particulate matter from oil-fired steam generating units have been promulgated in the Federal Register. Method 19A has been incorporated into Method 19 and is published with these standards.

b. Industrial Surface Coating; Plastic Parts for Business Machines. Promulgated 1/29/88 (53 FR 2672). The standards require affected facilities to limit VOC emissions to no more than 1.5 kg/liter of coating solids applied for prime and color coats and to nore more than 2.5 kg/liter of coating solids applied for texture and touch-up coats.

c. Residential Wood Heaters. Promulgated 2/26/88 (53 FR 5860). Standards for these affected facilities have been promulgated. Certification of wood heaters are based on certifying an entire model line.

TECHNICAL NOTES

1. Training and Seminars.

a. Fugitive VOC Leak Detection, April 5-6, 1988. Contents: Fugitive VOC leak detection, organic chemistry review, portable VOC instruments, measurement, data and auditing. Contact: Kay Howard, Registrar (919-541-4350).

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SUMMARY OF EPA TEST METHODS

Method		Reference		Description
1-8		42 FR 41754	08/18/77	Velocity, Orsat, PM, SO_2, NO_x, etc.
		43 FR 11984	03/23/78	Corr. and amend. to M-1 thru 8.
1-24	C	52 FR 34639	09/14/87	Technical corrections
		52 FR 42061	11/02/87	Corrections.
1		48 FR 45034	09/30/83	Reduction of number of traverse points.
1	R	51 FR 20286	06/04/86	Alternative procedure for site selection.
2A		48 FR 37592	08/18/83	Flow rate in small ducts - vol. meters.
2B		48 FR 37594	08/18/83	Flow rate - stoichiometry.
3A		51 FR 21164	06/11/86	Instrumental method for O_2 and CO_2.
3R		48 FR 49458	10/25/83	Addition of QA/QC.
4	R	48 FR 55670	12/14/83	Addition of QA/QC.
5	R	48 FR 55670	12/14/83	Addition of QA/QC.
5	R	45 FR 66752	10/07/80	Filter specification change.
5	R	48 FR 39010	08/26/83	DGM revision.
5	R	50 FR 01164	01/09/85	Incorp. DGM and probe cal. procedures.
5	R	52 FR 09657	03/26/87	Use of critical orifices as cal stds.
		52 FR 22888	06/16/87	Corrections.
5A		47 FR 34137	08/06/82	PM from asphalt roofing (P as M-26).
5A	R	51 FR 32454	09/12/86	Addition of QA/QC.
5B		51 FR 42839	11/26/86	Nonsulfuric acid particulate matter.
5D		49 FR 43847	10/31/84	PM from baghouses.
5D	R	51 FR 32454	09/12/86	Addition of QA/QC
5E		50 FR 07701	02/25/85	PM from fiberglass plants.
5F		51 FR 42839	11/26/86	PM from FCCU.
5G		53 FR 05860	02/26/88	PM from Woodstove - Dilution Tunnel
5H		53 FR 05860	02/26/88	PM from Woodstove - Stack
6	R	49 FR 26522	06/27/84	Addition of QA/QC.
6	R	48 FR 39010	08/26/83	DGM revision.
6	R	52 FR 41423	10/28/87	Use of critical orifices for FR/Vol meas.
6A		47 FR 54073	12/01/82	SO_2/CO_2.
6B		47 FR 54073	12/01/82	Auto SO_2/CO_2.
6A/B	R	49 FR 09684	03/14/84	Incorp. coll. test changes.
6A/B	R	51 FR 32454	09/12/86	Addition of QA/QC.
6C		51 FR 21164	06/11/86	Instrumental method for SO_2.
		52 FR 18797	05/27/87	Corrections.
7	R	49 FR 26522	06/27/84	Addition of QA/QC.
7A		48 FR 55072	12/08/83	Ion chromatograph NO_x analysis.
7B		50 FR 15893	04/23/85	UV NO_x analysis for nitric acid plants.
7C		49 FR 38232	09/27/84	Alkaline permanganate/colorimetric for NO_x.
7D		49 FR 38232	09/27/84	Alkaline permanganate/IC for NO_x
7E		51 FR 21164	06/11/86	Instrumental method for NO_x.
9		39 FR 39872	11/12/74	Opacity.
9A		46 FR 53144	10/28/81	Lidar opacity. Called Alternative 1.

10		39 FR 09319	03/08/78	CO.
10A		52 FR 30674	08/17/87	Colorimetric method for PS-4.
		52 FR 33316	09/02/87	Correction notice.
11		43 FR 01494	01/10/78	H_2S.
12		47 FR 16564	04/16/82	Pb.
12	R	49 FR 33842	08/24/84	Incorp. method of additions.
13A		45 FR 41852	06/20/80	F, colorimetric method.
13B		45 FR 41852	06/20/80	F, SIE method.
		45 FR 85016	12/24/80	Corr. to M-13A and 13B.
14		45 FR 44202	06/30/80	F from roof monitors.
15		43 FR 10866	03/15/78	TRS from petroleum refineries.
15A		52 FR 20391	06/01/87	TRS alternative/oxidation.
16		43 FR 07568	02/23/78	TRS from kraft pulp mills.
16	R	43 FR 34784	08/07/78	Amend. to M-16, H_2S loss after filters.
16	R	44 FR 02578	01/12/79	Amend. to M-16, SO_2 scrubber added.
16A		50 FR 09578	03/08/85	TRS alternative.
16A	R	52 FR 36408	09/29/87	Cylinder gas analysis alternative method.
16B		52 FR 36408	09/29/87	TRS alternative/GC analysis of SO_2.
		53 FR 02914	02/02/88	Corrections 16A/B.
17		43 FR 07568	02/23/78	PM, in-stack.
18		48 FR 48344	10/18/83	VOC, general GC method.
18	C	49 FR 22608	05/30/84	Corrections to Method 18.
18	R	52 FR 05105	02/19/87	Revisions to improve method
		52 FR 10852	04/03/87	Corrections
19		44 FR 33580	06/11/79	F-factor, coal sampling.
19	R	Tentative		Rewrite; combine with Method 19A.
19	R	48 FR 49460	10/25/83	Corr. to F factor equations and F_c value.
19	R	52 FR 47853	12/16/87	M-19A incorp. into M-19.
20		44 FR 52792	09/10/79	NO_x from gas turbines.
20	R	47 FR 30480	07/14/82	Corr. and amend.
20	R	51 FR 32454	09/12/86	Clarifications.
21		48 FR 37598	08/18/83	VOC leaks.
21	Corr.	49 FR 56580	12/22/83	Corrections to Method 21.
22		47 FR 34137	08/06/82	Fugitive VE.
22	R	48 FR 48360	10/18/83	Add smoke emission from flares.
23		Open		
24		45 FR 65956	10/03/80	Solvent in surface coatings.
24A		47 FR 50644	11/08/82	Solvent in ink (P as M-29).
25		45 FR 65956	10/03/80	TGNMO.
25	R	53 FR 04140	02/12/88	Revisions to improve method.
25A		48 FR 37595	08/18/83	TOC/FID.
25B		48 FR 37597	08/18/83	TOC/NDIR.

26	Open		
27	48 FR 37597	08/18/83	Tank truck leaks.
28	53 FR 05860	02/26/88	Woodstove certification.
28A	53 FR 05860	02/26/88	Air to fuel ratio.
101	47 FR 24703	06/08/82	Hg in air streams.
101A	47 FR 24703	06/08/82	Hg in sewage sludge incinerators.
101 R	49 FR 35768	09/12/84	Corrections to M-101 and 101A.
102	47 FR 24703	06/08/82	Hg in H_2 streams.
103	48 FR 55266	12/09/83	Revised Be screening method.
104	48 FR 55268	12/09/83	Revised Beryllium.
105	40 FR 48299	10/14/75	Hg in sewage sludge.
105 R	49 FR 35768	09/12/84	Revised Hg in sewage sludge.
106	47 FR 39168	09/07/82	Vinyl chloride.
107	47 FR 39168	09/07/82	VC in process streams.
107 R	52 FR 20397	06/01/87	Alternative calibration procedure.
107A	47 FR 39485	09/08/82	VC in process streams.
108	51 FR 28035	08/04/86	Inorganic arsenic.
108A	51 FR 28035	08/04/86	Arsenic in ore samples.
111	50 FR 05197	02/06/85	Polonium-210
PS-1	48 FR 13322	03/30/83	Opacity.
PS-2	48 FR 23608	05/25/83	SO_2 and NO_x.
PS-3	48 FR 23608	05/25/83	CO_2 and O_2.
PS-4	50 FR 31700	08/05/85	CO.
PS-5	48 FR 32984	07/20/83	TRS.
App-F	52 FR 21003	06/04/87	Quality Assurance for CEMS.

Alternative Procedures and Misc.

48 FR 44700	09/29/83	S-Factor Method for Sulfuric Acid Plants.
48 FR 48669	10/20/83	Corrections to S-Factor publ.
49 FR 30672	07/31/84	Add fuel analysis procedures for gas turbines.
51 FR 21762	06/16/86	Alternative PST for low level concentrations.

Summary of Proposed EPA Test Methods

1A		48 FR 48955	10/21/83	P	Traverse points in small ducts.
2C		48 FR 48956	10/21/83	P	Flow rate in small ducts - std. pitot.
2D		48 FR 48957	10/21/83	P	Flow rate in small ducts - rate meters.
5C		Tentative			PM from small ducts.
5F	R	52 FR 08476	03/18/87	P	Barium titration procedure.
7A	R	Tentative			Revisions.
9B		Tentative			Transmissometer.
10	R	52 FR 32026	08/25/87	P	Alternative trap.
10	R	Tentative			Tank collection.
10B		52 FR 32026	08/25/87	P	GC method for PS-4.
15	R	Tentative			Revisions.
16	R	Tentative			Revisions.
PS-6		52 FR 0718	03/09/87	P	Velocity and Mass Emission Rate.
108B		Tentative			Arsenic alternative.
108C		Tentative			Arsenic in ore alternative.
108D		Tentative			Arsenic in ore alternative.
109		52 FR 13600	04/23/87	P	Coke oven VE.
xxx		Tentative			Chromium - Hexavalent and Total.
xx		Tentative			Misc. revisions to Appendix A, 40 CFR Part 60.
Part 60		53 FR 05082	02/19/88	P	Test Methods & Procedures Revisions (40 CFR 60)
F-2		Tentative			PM-10 (EGR Procedure).
F-2A		Tentative			PM-10 (CFR Procedure).
Part 61		Tentative			Corrections.
9	R	50 FR 24770	06/13/85	D	Amendment to Method 9.
19A		48 FR 48964	10/21/83	D	30-day rolling average for SO_2.
23		45 FR 39766	06/11/80	D	Halogenated organic carbon.
110		45 FR 26660	04/18/80	D	Benzene.
		50 FR 25095	06/17/85	D	Alternative monitoring procedure for KPM.

P = Proposal
D = Dropped
Tentative = Under evaluation

DETERMINATION OF METHOD 6 SAMPLES IN THE PRESENCE OF AMMONIA

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Introduction

The interference effects of ammonia (NH_3) on the collection and analysis of Method 6 samples have been known for some time. Free NH_3 reacts with sulfur dioxide (SO_2) to form sulfite in the probe and isopropanol (IPA) scrubber. Ammonia that reaches the peroxide solution and is dissolved, also reacts with the thorin indicator. Method 6 cautions testers of this potential for interference and requires the use of acceptable alternative procedures for handling its effects; however, no guidance to appropriate methodology is given.

Techniques have been studied and tested in the laboratory that minimize the reaction of NH_3 and SO_2 in the probe and remove the interferences produced in the collection impingers. Alternative procedures are recommended for Method 6 for testing at sources where NH_3 is suspected to be an interferent.

Background and Approaches

The literature revealed two basic approaches to resolving the NH_3 interference problem: (1) remove NH_3 during sampling using a heated probe and filter in conjunction with an NH_3 scrubber, and (2) remove or correct the NH_3 effects after collecting the sample.

Reactions between NH_3 and SO_2 in the sample stream can occur at temperatures below approximately 235°C. Heating the probe to 275°C generally can quench the reactions by keeping the NH_3 in an unstable state. However, if particulate ammonium sulfite is present in the gas stream, it will decompose at this temperature and liberate SO_2 to bias the sample results high. A high efficiency in-stack filter, similar to the one recommended by the method to trap very fine metallic fumes, would be needed to prevent this particulate from entering the probe.

For the NH_3 scrubber, two candidate solutions were recommended in the literature for use in place of the IPA. One used 3 N hydrochloric acid (HCl), and the other employed an 80:20 mixture of isopropanol:1 N HCl; the rationale for these choices being that an acidic solution would trap NH_3 while allowing most of the SO_2 to pass through. Any residual SO_2 trapped by the scrubbers could possibly be recovered during the 15-minute post-sampling purge.

Removal of the interference effects from samples collected in an unmodified train were also researched. This approach involved the analysis of peroxide and IPA sample fractions after pretreatment to remove NH_3. Initial experiments to remove NH_3 collected with the sample by heated evaporation and by ion exchange proved unsuccessful. Subsequent analyses focused on quenching the effects of the dissolved NH_3 by converting to a noninterfering state and oxidizing the trapped sulfite to sulfate before analysis.

Testing and Discussion

I. Ammonia Removal During Sampling.

The test system is shown in Figure 1. Excess SO_2 gas was generated at 166 and 314 ppm from gas cylinders. Concentrated ammonia gas was introduced into the gas stream at flow rates that would result in the appropriate dilution by the sample gas. The volume of NH_3 introduced was regulated by a flow controller that had been calibrated against a bubble

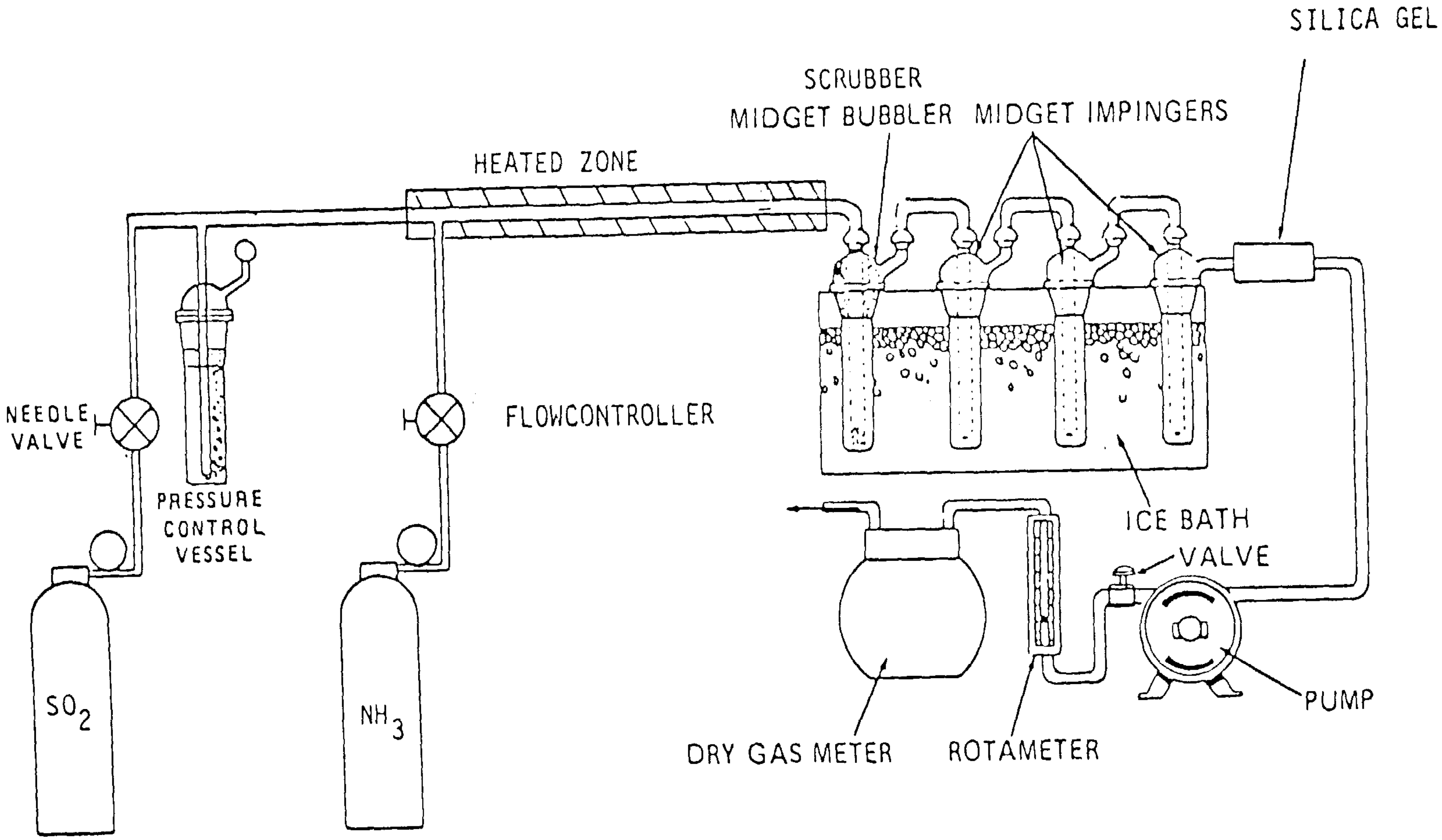

Figure 1. Laboratory setup

flowmeter. The excess SO_2 was vented upstream of the probe to prevent NH_3 loss. The NH_3 concentrations in the samples were varied between 50-500 ppm.

Before initiating the test, the experimental NH_3 scrubbers, analytical reagents, SO_2 cylinder gases, and analyst's technique were evaluated. Liquid audit samples were used to evaluate the analyst's technique and analytical reagents. Method 6 was used to verify the cylinder gas tag values. The results are listed in Table 1 and show good operator technique and accurate tag concentrations.

TABLE 1. Preliminary Evaluations

I. Liquid SO_2 Audits

Sample number	Known conc.	Analyzed conc.	Percent relative accuracy
1	338 ppm	336 ppm	0.6
2	364	361	0.8

II. Analysis of SO_2 Cylinder Gases

Tag value	Analyzed conc.	Percent recovered
166 ppm	157 ppm	95
	160	96
	159	96
314 ppm	309	98
	286	91
	312	99
	307	98
	298	95
	311	99

The two scrubbing solutions were shown to be efficient removers of NH_3 by passing high concentrations of NH_3 through the scrubbers while using a backup phenolpthalein solution as a breakthrough indicator. Stoichiometric calculations indicated that both scrubbers contained a large excess absorption capacity. However, the 3 M HCl scrubber was subsequently removed from consideration when it was found that chloride solution carryover into the peroxide impingers produced a cloudy titration endpoint which biased SO_2 recoveries 5-10 percent high.

Samples were collected using the Method 6 train with the IPA:HCl scrubber and probe modifications in place. Table 2 shows that good recoveries were obtained for 166 and 314 ppm samples containing no NH_3. When NH_3 was added, recoveries dropped by up to 66 percent and thus showed the modifications to be ineffective.

The individual train components were investigated to determine the point of sample loss. Spent scrubber solution was titrated to check for sulfite capture, but the high chloride concentration prevented an accurate analysis. One reaction product between SO_2 and NH_3 is white particulate matter. When transparent Teflon tubing was substituted for the steel probe, no visible particulate formation was observed upstream of the scrubber

TABLE 2. Effect of Ammonia on Modified Sampling Train

Without Ammonia

SO_2 conc.	Analyzed conc.	Percent recovered
166 ppm	157 ppm	95
	160	96
	159	96
314 ppm	309	98
	286	91
	312	99
	307	98
	298	95
	311	99

With Ammonia

SO_2 conc.	NH_3 conc.	Analyzed conc.	Percent recovered
166 ppm	64 ppm	162 ppm	97
	69	161	97
	299	73	44
	455	108	65
314 ppm	139	259	82
	158	261	83
	159	251	80
	163	314	100
	181	305	97
	224	239	76
	232	267	85

impinger. Analysis of the probe wash after numerous samples had been collected showed no evidence of sulfate collection in the probe.

A faint white condensation was observed in the impinger stems of some samples with low recoveries. It appeared that particulate matter was forming on the interior surface of the stems aided by water droplets remaining from previous sample recovery washes. Further sampling was done with impingers having dry stems. Some success resulted from this as can be seen in Table 3. In the two worst cases, a white condensate was noticed after sampling despite using dry stems and dry cylinder gases. Analysis of stem washes revealed that only a small portion of the total unrecovered SO_2 was trapped at this point.

II. Removal of Interference Effects After Sampling.

All indicators suggested that the unrecovered SO_2 was being trapped in the NH_3 scrubber. Because the scrubber solution could not be directly titrated, the possibility of replacing the scrubber solution and treating samples containing collected NH_3 was investigated. The NH_3 scrubber was replaced with the standard IPA impinger in subsequent

TABLE 3. Impinger Stem Condensation

Dry Stems SO_2 conc.	NH_3 conc.	Analyzed conc.	Percent recovered
314 ppm	188 ppm	312 ppm	99
	185	309	99
166 ppm	64	162	97
	69	161	97
	299	73	44*
	455	108	65*
	494	133	80*

*White condensate in stems

tests, and emphasis was placed on removing NH_3 from the collected sample followed by analysis of the IPA and peroxide fractions.

Ammonia dissolved in a solution can usually be evaporated with gentle heating. To test this, the contents of the IPA and peroxide impingers were mixed and made basic to convert any NH_4^+ to NH_3, followed by gentle heating. Analysis showed the interference to still be present. Attempts to remove NH_3 as NH_4^+ using a Dowex 50W-X8 cation resin proved only partially effective and was time-consuming.

A report by Fritz and Yamamura indicated that only free NH_3, and not NH_4^+, interferes with the thorin titration. This was shown to be the case by acidifying the sample to favor the NH_4^+ state prior to sample titration. The low and inconsistent results that had been experienced due to interference effects were eliminated following this treatment. The addition of 0.5 ml 1 N HCl to the combined impinger contents was sufficient to convert dissolved NH_3 to NH_4^+ without creating an excess of chloride to hinder the clarity of the titration endpoint.

With the effects of dissolved NH_3 thus resolved, means of analyzing the SO_2 trapped in the IPA scrubber were sought. Sources disagree as to the reaction products of NH_3 and SO_2 in IPA. Since only sulfate is detected in the analysis titration, ion chromatography was used to determine whether SO_2 existed in the sulfite or sulfate state. Analyses revealed sulfite to be the overwhelming specie present. Analysis by Method 6 confirmed these results. Initial titrations revealed that only an average 2.4 percent of the sample is trapped as sulfate in the IPA. Upon adding peroxide to the IPA fraction and retitrating, previously undetected sulfite was oxidized to sulfate and yielded an average of 96 percent of the remaining sample. With NH_3 present, only a small portion (2 percent) of the SO_2 passed through the IPA to be collected in the peroxide impingers. These data are shown in Table 4. Upon combining the IPA and peroxide impinger contents, followed by acidification to convert dissolved NH_3 to NH_4^+, the entire sample could be titrated without interference effects (Table 5).

In light of the IPA impinger functioning primarily in removing sulfur trioxide (SO_3) interference, the utility of analyzing SO_2 trapped by NH_3 in the IPA hinges upon performing separate titrations of the IPA and peroxide sample fractions. The IPA fraction would have to be titrated twice to determine the amount of SO_2 collected by difference. Sulfur

TABLE 4. SO_2 Distribution in the Presence of NH_3

Sample concentration ppm SO_2	ppm NH_3	SO_4^- in IPA (percent)	SO_3^- in scrubber (percent)	SO_2 reaching H_2O_2 impingers (percent)
344	414	2.5	89	7.6
	421	1.2	98	0.4
	421	3.5	97	0
	419	2.6	97	0.8
	463	2.1	97	1.3
Average		2.4	96	2.0

TABLE 5. Combined Impinger Analysis After Correction for NH_3

Generated concentrations ppm SO_2	ppm NH_3	SO_2 found (ppm)	Collection efficiency (percent)
344	456	333	97
	448	343	100
	453	319	93
	448	345	100
	445	343	100
	426	343*	100
	432	346*	101
	451	328*	95

*IPA impinger spiked with sulfuric acid

trioxide is collected and oxidized to sulfate in the IPA impinger, whereas SO_2 will be trapped as sulfite. This allows for double titration, but a small negative bias (average 2.4 percent) would result from the small fraction of SO_2 oxidized to sulfate in the IPA and counted with the SO_3 fraction. For three samples where the IPA solutions were spiked with sulfuric acid at an equivalent stack concentration of 20 ppm, SO_2 concentrations by differential titration resulted in recoveries of 100, 101, and 95 percent (Table 5).

Recommended Procedures

With the appropriate measures taken, Method 6 samples from sources having NH_3 emissions can be collected and analyzed accurately. Method 6 should be amended to require the following procedures when testing at such facilities.

1. The probe should be maintained at a temperature of at least 275°C.

2. A high-efficiency filter should be used at the probe tip.

3. All impinger contents should be combined for analysis. The IPA impinger stems should be rinsed into the sample container, and 0.5 ml of 0.1 N HCl added before the titration.

4. If SO_3 is present in the gas stream, the IPA and peroxide fractions should be titrated separately. The 0.5 ml of HCl should be added to each fraction. After initially titrating an aliquot of the IPA fraction for SO_3, another aliquot is taken and 5 ml of 3 percent hydrogen peroxide is added for SO_2 analysis. This SO_2 fraction, plus the peroxide fraction, constitutes the sample.

If no determination of the SO_2/SO_3 split is necessary, then Step 4 need not be regarded.

References

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