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NMAM Methods Update: A Laboratory Response to Concerns About Technologically Outdated and Problematic Methods

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The National Institute for Occupational Safety Health (NIOSH) publishes the NIOSH Manual of Analytical Methods (NMAM). *The NMAM, although subject to various revisions and the incorporation of supplemental editions over the years, still contains many methods that are technologically outdated or problematic, as identified in a recent survey of the various users of the NMAM. Whereas the survey identified a number of problematic methods based on various chromatographic techniques, those selected for inclusion in this project employed analysis by gas chromatography (GC). The GC methods selected for evaluation were categorized as Phases 1, 2, 3, and 4 based on necessity as determined by the results of the client survey or internal assessment. The Phase 1 methods included: NMAM 1606 (Acetonitrile), NMAM 2005 (Nitroaromatic Compounds), and NMAM 1453 (Vinyl Acetate); the Phase 2 methods: NMAM 1003 (Halogenated Hydrocarbons), NMAM 1501 (Aromatic Hydrocarbons), NMAM 2555 (Ketones I), and NMAM 1403 (Alcohols IV); the Phase 3 methods: NMAM 2552 (Methyl Acrylate), NMAM 2537 (Methyl and Ethyl Methacrylate), and NMAM 2553 (Ketones II), and the Phase 4 methods: NMAM 2556 (Isophorone), NMAM 1460 (Isopropyl Acetate), and NMAM 1618 (Isopropyl Ether).*

All methods previously specifying packed column chromatography have been evaluated using the appropriate fused silica capillary column. Improvements in individual analyte desorption efficiencies were achieved at concentrations substantially lower than those used in the previous methods. Most analytes evaluated had their respective limit of detection lowered by a factor of ten-to twentyfold. Thirty-day storage stability studies, previously lacking in a number of methods or for new analytes, were successfully completed to meet current method development criteria. Additional benefits resulting from this effort included the incorporation of single analyte methods into chemically related multianalyte methods and the evaluation of certain isomers, such as the methylstyrenes and xylenes, which previously could not be separated.

Keywords gas chromatography, NIOSH, NMAM

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The National Institute for Occupational Safety and Health (NIOSH) publishes the *NIOSH Manual of Analytical Methods (NMAM)*, a primary reference that has been a reliable source of analytical methods used in occupational health laboratories throughout the world for over 25 years.(1) The NMAM, despite several revisions and supplements over the years, contains many methods that are technologically outdated. In addition, various NMAM users have noted that some of the methods are problematic or totally nonfunctional. In an effort to address this situation, the NMAM editor conducted a survey of the various NMAM clients. The survey results identified a number of problematic methods based on various chromatography techniques that required either substantial modifications or new method development.(2) The methods selected for evaluation at the start of this project were based on outdated or ineffective gas chromatography (GC) analyses and procedures. The resulting laboratory research criteria and protocols for method development were based on the NIOSH *Guidelines for Air Sampling and Analytical Method Development and Evaluation*.(3)

At the start of this project, each GC method was categorized based on client need as indicated by the results of the NMAM survey as well as internal assessment. The Phase 1 methods included: NMAM 1606 (Acetonitrile), NMAM 2005 (Nitroaromatic Compounds), and NMAM 1453 (Vinyl Acetate); the Phase 2 methods: NMAM 1003 (Halogenated Hydrocarbons), NMAM 1501 (Aromatic hydrocarbons), NMAM 2555 (Ketones I), and NMAM 1403 (Alcohols IV); the Phase 3 methods: NMAM 2552 (Methyl Acrylate), NMAM 2537 (Methyl and Ethyl Methacrylate), and NMAM 2553 (Ketones II); and the

Phase 4 methods: NMAM 2556 (Isophorone), NMAM 1460 (Isopropyl Acetate), and NMAM 1618 (Isopropyl Ether).

In addition to correcting any problems associated with the individual methods, a number of other improvements were incorporated into the method development research. First, those methods that were based on packed column chromatography were evaluated using capillary column chromatography. Furthermore, the use of capillary column chromatography and improvements in instrumentation allowed the limit of detection (LOD) and limit of quantitation (LOQ) to be lowered for each analyte evaluated. Another goal was to improve desorption efficiency (DE) through solvent modifications. For some analytes, new or additional desorption efficiency studies were required to meet the current method development criteria of at least 75% recovery.(3) Other analytes required DE studies at levels substantially lower (5× LOQ to approximately 0.1× recommended exposure level [REL] or permissible exposure level [PEL]) than were evaluated in the original method in order to more realistically evaluate current occupational exposure levels.

Additionally, during each initial packed column method development, the DEs were determined separately for each analyte. Because most of the past DE studies do not represent actual occupational exposure scenarios where a number of different analytes may be collected on a single solid sorbent tube, DE studies were conducted with each sorbent tube containing multiple analytes. Also, due to current capillary column technology, it was possible to combine some single analyte methods into methods containing an analogous series of analytes (i.e., methyl ethyl ketone was added to the Ketones I method [NMAM 2555] and trichloroethylene was added to the Halogenated Hydrocarbons method [NMAM 1003]). To successfully achieve these objectives and meet the method development crieteria,(3) some of the methods required evaluation using alternative solid sorbent media and/or a different desorption solvent. New method development efforts were required for a few of the outdated methods to satisfy the current method development criteria.

Finally, after a review of all the methods, it was determined that most lacked sufficient storage stability data to comply with the current method development criteria of 30 days.(3) Thus, this article will endeavor to provide a comparison of the new or modified methods versus the outdated and/or problematic packed column methods.

RESULTS AND DISCUSSION

For methods with a small number of chemical analytes, a table is provided containing data that compare the differences between capillary columns and packed columns, sorbent and solvent/solvent systems used, as well as the limits of detection, desorption efficiency recoveries, and the storage stability studies at 30 days. The new methods consist of either technologically updated draft methods currently in review for the next NMAM supplement, or they describe methods published in the current edition of the NMAM.(1) These new methods are being evaluated to replace the outdated methods from prior editions and supplements of the NMAM. For those methods lacking data that are currently required for method development efforts, the results are expressed as "not determined" (ND) in the table.

Phase 1 Methods

Three Phase 1 methods identified by the NMAM survey have been addressed. LOD, DE, and storage stability improvements for these methods (NMAM 1606, 2005, and 1453) are summarized in Table I. The first method, NMAM 1606 (Acetonitrile), represents an entirely new method development in which the combination of using a Stabilwax capillary column (Restek, Bellafonte, Pa.) and a methylene chloride/methanol (85:15) desorbing solvent improved recovery from 81% to 101.9%. This improved recovery was achieved at much lower concentrations as illustrated in Table I.

The second method development effort of the Phase 1 group to be completed was NMAM 2005 (Nitroaromatic Compounds). The analytes in this method include nitrobenzene, o-nitrotoluene, m-nitrotoluene, p-nitrotoluene, and 1-chloro-4-nitrobenzene. A 30-m Rtx-5 Amine fused silica capillary column (Restek) allowed for the resolution and subsequent analysis of the three nitrotoluene isomers. Both the original packed column method and the new method employ silica gel sorbent tubes and methanol as the desorption solvent.

The final method development completed in the initial phase of the NMAM update project was NMAM 1453 (Vinyl Acetate).(4) The new method employs an Rtx-5 capillary column (Restek) and methylene chloride/methanol (95:5) as the desorbing solvent and includes a 30-day storage stability study. DataChem Laboratories, Inc. completed this method development in support of the NMAM update project.

Phase 2 Methods

Four methods were evaluated in the second phase of this project: NMAM 1501, NMAM 2555, NMAM 1403, and NMAM 1003. The first method evaluated, NMAM 1501 (Aromatic Hydrocarbons), includes benzene, toluene, ethylbenzene, o-xylene, m-xylene, p-xylene, cumene, p-*tert*-butyltoluene, α-methylstyrene, β-methylstyrene, and styrene. Vinyl toluene, an analyte included in the original method, was dropped from the method because a standard could not be obtained. Likewise, naphthalene was omitted from the revised method because it failed to meet the required criteria of 75% recovery at all levels evaluated. β-methylstyrene and the xylene isomers, which were not resolved in the original method, are new additions to the method. In order to obtain baseline resolution of all the analytes in this method, two columns were utilized: Stabilwax and Rtx-35 fused silica capillary columns (Restek). Both resolved and separated all analytes, which were divided into two groups (A and B) based on the column used for the analysis. Anasorb CSC (SKC, Inc., Eighty Four, Pa.) was used as the solid sorbent media for the evaluation, although Anasorb 747 (SKC, Inc.) was also evaluated and performed equally as well. Anasorb CSC was used because

TABLE I. Comparison of New and Previous Phase 1 Methods

Analyte (NMAM Method No.)	Column[A]	Sorbent	Solvent	LOD (μg/sample)	DE (%) (range studied in μg/sample)	30-Day Storage Stability (%)
Acetonitrile						
1606 New	Stabilwax (30 m)	Anasorb CSC[B]	Methylene Chloride/ Methanol (85:15)	0.8	101.9 (39–275)	98.5
1606 Original	Packed	Anasorb CSC	Benzene	10	81 (346–1383)	ND
Nitrobenzene						
2005 New	Rtx-5 Amine (30 m)	Silica gel	Methanol	0.6	98.7 (60–289)	100.2
2005 Original	Packed	Silica gel	Methanol	20	100 (120–480)	ND
o-Nitrotoluene						
2005 New	Rtx-5 Amine (30 m)	Silica gel	Methanol	0.8	98.2 (58–291)	101.2
2005 Original	Packed	Silica gel	Methanol	0.8	103 (300–1200)	ND
m-Nitrotoluene						
2005 New	Rtx-5 Amine (30 m)	Silica gel	Methanol	1.0	97.5 (58–289)	99.4
2005 Original	Packed	Silica gel	Methanol	ND	ND	ND
p-Nitrotoluene						
2005 New	Rtx-5 Amine (30 m)	Silica gel	Methanol	2.6	96.9 (51–255)	99.4
2005 Original	Packed	Silica gel	Methanol	ND	ND	ND
1-Chloro-4-nitrobenzene						
2005 New	Rtx-5 Amine (30 m)	Silica gel	Methanol	2.5	100.3 (60–298)	97.6
2005 Original	Packed	Silica gel	Methanol	0.1	103 (25–100)	ND
Vinyl acetate						
1453 New	Rtx-5 (30 m)	ORBO 92[C]	Methylene Chloride/ Methanol (95:5)	1	98.5 (3–1120)	93
1453 Original (OSHA #51)	Packed	Carbon molecular sieve[D]	Methylene Chloride/ Methanol (95:5)	1	95.3[E] (187–710)	ND

[A] Stabilwax and Rtx columns are products of Restek.
[B] All Anasorb sorbents were obtained from SKC, Inc.
[C] Sorbent obtained from Supelco (Bellefonte, Pa.).
[D] OSHA method used Ambersorb XE-347 tubes which are no longer being manufactured.
[E] The packed column method for vinyl acetate was adapted from OSHA Method No. 51 from which the desorption efficiency was based.(4)

of its history of recovery data. Each sorbent tube was desorbed with 1 mL of carbon disulfide solvent. Acceptable analyte recovery was achieved at substantially lower analyte concentrations than the DE recovery levels reported in the original method.

For example, in the original method, benzene had a DE recovery of 96.4% at the 88 μg level, and α-methylstyrene had a DE recovery of 91.4% at the 687 μg level. In the updated method, benzene and α-methylstyrene had recoveries of 92.8% at the 4 μg level and 93.2% at the 36 μg level, respectively. Styrene failed the current laboratory method development guidelines criteria at the levels evaluated in this method development (5× LOQ to 0.1× REL/PEL). However, styrene met the original DE criteria at levels 0.5×, 1.0×, and 2.0× the REL/PEL. Styrene was included in the new method with these restrictions noted.

Substantial improvement in the individual LODs was achieved for all analytes in the revised Aromatic Hydrocarbons method (NMAM 1501), ranging from 0.4 μg/sample for styrene to 1.1 μg/sample for p-*tert*-butyltoluene, whereas, in the original packed column method, the LOD was reported as 10 μg/sample for all analytes. A 30-day storage stability study, absent in the original method, was completed for each analyte. All analytes, again with the exception of styrene at the low level studied (91 μg), were stable for 30 days, with recoveries ranging from 96% for α-methylstyrene, β-methylstyrene, and p-*tert*-butyltoluene to 104% for toluene and m-xylene.

The second method evaluated in Phase 2 was NMAM 2555 (Ketones I). This method includes acetone, methyl ethyl ketone, 2-pentanone, methyl isobutyl ketone, 2-hexanone, diisobutyl ketone, and cyclohexanone. This evaluation focused on using an alternative solid sorbent to improve recovery. The selection of Anasorb CMS sorbent tubes (SKC, Inc.), allowed for the inclusion of methyl ethyl ketone (MEK), previously single analyte method NMAM 2500, in the new Ketones I method. Unlike activated charcoal sorbent, Anasorb CMS sorbent is inert to MEK, allowing for high recoveries and acceptable storage stability results.

The third method evaluated in this group was NMAM 1403 (Alcohols IV), which consisted of the analytes 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol. All of the analytes were resolved using a Stabilwax-DA fused silica capillary column (Restek). Analytes were collected on Anasorb CSC, and methylene chloride/methanol (95:5) was used as the desorption solvent. Whereas the actual percentage of DE recoveries achieved in this method development were not notably different from those reported in the original packed column method, it should be noted that the results for the current method development were achieved at substantially lower analyte concentrations (36–48 μg). Table II highlights the differences and improvements in NMAM 2555 and NMAM 1403 resulting from new and updated GC methodologies.

The final method evaluated in the Phase 2 series was NMAM 1003 (Halogenated Hydrocarbons). The analytes included in this method development were benzyl chloride, bromochloromethane, 1,1-dichloroethane, 1,1,1-trichloroethane, trichloroethylene, chloroform, 1,2-dichloroethylene, tetrachloroethylene (perchloroethylene), carbon tetrachloride, o-dichlorobenzene, p-dichlorobenzene, 1,2-dichloroethane, 1,1,2-trichloroethane, chlorobenzene, 1,2,3-trichloropropane, hexachloroethane, and bromoform. Trichloroethylene, previously a single analyte method (NMAM 1022) and inadvertently left out of the printed method, was incorporated into the new method because of improved column technology. Because of the large number of analytes in this method, the use of both an Rtx-502.2 and Rtx-35 fused silica capillary columns (Restek) was required for the resolution and separation of all the analytes. Two columns were required because no single column evaluated could achieve baseline separation of all analytes. The analytes were divided into two groups (A and B) based on which column was selected for the analysis.

An additional reason for the separation of the analytes into two groups was that previous laboratory investigations had shown that in most instances, when more than eight analytes are collected on a single sorbent tube, the individual recovery results for each analyte were diminished. The degree of reduction in DE is independent of the combination of the analytes present.

Analytes were collected on Anasorb CSC, and 1 mL carbon disulfide was used as the desorption solvent. Overall, the average DE results were slightly improved (92–101% recovery) for each analyte evaluated when compared with those listed in the original packed column method. As noted in previous methods, the results are more significant because for most analytes they were achieved at substantially lower concentrations. Some examples of this improvement in DE recovery at lower analyte concentrations include tetrachloroethylene and o-dichlorobenzene, which had a DE recovery of 96% over the range of 2100 to 8000 μg and 86% over the range of 500 to 1900 μg, respectively, in the original packed column method.

In contrast, as reported in the updated method, tetrachloroethylene exhibited an average DE of 95% over the concentration range of 8 μg to 194 μg (25× to 40× lowest level) and o-dichlorobenzene demonstrated an average DE of 94% over the range of 19 to 424 μg (5× to 25× lower level). Similar improvements in the LODs for each analyte were achieved in the new method where they ranged from 0.6 μg/sample for chlorobenzene and trichloroethylene to 6.0 μg/sample for bromoform when compared with the reported LOD of 10 μg/sample for all analytes in the original packed column method.

A 30-day storage stability study, although not performed in the original method, was conducted as part of this method development effort. All the analytes, with the exception of bromoform were stable for 30 days, with recoveries ranging from 88% for bromochloromethane to 104% for o-dichlorobenzene. Bromoform was stable for 14 days (101%), but the recovery dropped to 77% after 30 days.

Phase 3 Methods

After the completion of the Phase 2 methods in the NMAM update project, continuing research was directed to those methods designated as Phase 3 based on the NMAM survey and the opinion of other science professionals. Phase 3 methods include NMAM 2552, 2537, and 2553. Table III highlights the differences between the original and newly developed methods. The first method evaluated was NMAM 2552 (Methyl Acrylate). The LOD was improved from 10 μg/sample to 0.5 μg/sample through the use of capillary chromatography and improved instrumentation. Acceptable recoveries were obtained at lower concentration than those reported in the original method. A 30-day storage stability study was successfully completed (105%).

The second method evaluated was NMAM 2537 (Methyl and Ethyl Methacrylate). Ethyl methacrylate, not included in the original method, was added because of its analogous relationship to methyl methacrylate and because its analysis has been requested occasionally. The new method is based on capillary column chromatography (Rtx-35), XAD-2 (SKC, Inc.) as the solid sampling media and carbon disulfide as the desorption solvent.

The final method evaluated in this group was NMAM 2553 (Ketones II). The analytes included in this method development included 2-heptanone, 3-heptanone, 5-methyl-3-heptanone, mesityl oxide, and camphor. The new method is based on capillary column chromatography (Rtx-200, Restek), the use of Anasorb CMS sorbent tubes for sample collection, and 2% isopropanol in carbon disulfide as the desorption solvent. LODs were improved from 50 μg/sample in the original method to as low as 0.3 μg/sample for mesityl oxide.

Phase 4 Methods

The Phase 4 methods, determined from various sources, included NMAM 2556 (Isophorone), NMAM 1460 (Isopropyl Acetate), and NMAM 1618 (Isopropyl Ether). The first method selected for evaluation in this group was NMAM 2556 (Isophorone). In the original method, isophorone was collected on petroleum-based charcoal sorbent tubes, desorbed with 1 mL carbon disulfide, and analyzed using packed column chromatography. In the new method, isophorone is collected

TABLE II. Comparison of Select New and Previous Phase 2 Methods: NMAM 2555 and NMAM 1403

Analyte (NMAM Method No.)	Column[A]	Sorbent[B]	Solvent	LOD (μg/sample)	DE (%) (range studied in μg/sample)	30-Day Storage Stability Study (%)
Acetone						
2555 New	Rtx-35 (30 m)	Anasorb CMS	Carbon disulfide	0.9	98.2 (59–295)	100.7
1300 Original	Packed	Anasorb CSC	Carbon disulfide	20	86 (2400–14,200)	ND
Methyl ethyl ketone						
2555 New	Rtx-35 (30 m)	Anasorb CMS	Carbon disulfide	0.9	98.6 (60–300)	101.7
2500 Original[C]	Packed	Anasorb 747[D]	Carbon disulfide	4	103[E] (4000–18,000)	90[F]
2-Pentanone						
2555 New	Rtx-35 (30 m)	Anasorb CMS	Carbon disulfide	0.9	99.3 (61–305)	101.5
1300 Original	Packed	Anasorb CSC	Carbon disulfide	20	90 (3500–14,000)	ND
Methyl isobutyl ketone						
2555 New	Rtx-35 (30 m)	Anasorb CMS	Carbon disulfide	0.9	96.4 (56–280)	103.8
1300 Original	Packed	Anasorb CSC	Carbon disulfide	20	91 (2100–8300)	ND
2-Hexanone						
2555 New	Rtx-35 (30 m)	Anasorb CMS	Carbon disulfide	0.9	100.6 (61–305)	101.4
2555 Original	Packed	Anasorb CSC	Carbon disulfide	20	81 (1500–8100)	ND
Di-isobutyl ketone						
2555 New	Rtx-35 (30 m)	Anasorb CMS	Carbon disulfide	1	102.4 (59–295)	103.5
1300 Original	Packed	Anasorb CSC	Carbon disulfide	20	97 (1800–7000)	ND
Cyclohexanone						
2555 New	Rtx-35 (30 m)	Anasorb CMS	Carbon disulfide	1	95.4 (55–273)	87.4
1300 Original	Packed	Anasorb CSC	Carbon disulfide	20	82 (3800–18,000)	ND
2-Methoxyethanol						
1403 New	Stabilwax-DA (30 m)	Anasorb CSC	Methylene chloride/ Methanol (95:5)	0.8	97.8 (48–301)	103.8
1403 Original	Packed	Anasorb CSC	Methylene chloride/ Methanol (95:5)	10–20	98 (2000–8000)	ND
2-Ethoxyethanol						
1403 New	Stabilwax-DA (30 m)	Anasorb CSC	Methylene chloride/ Methanol (95:5)	0.7	100.2 (46–290)	105.0
1403 Original	Packed	Anasorb CSC	Methylene chloride/ Methanol (95:5)	10–20	102 (2000–7000)	ND
2-Butoxyethanol						
1403 New	Stabilwax-DA (30 m)	Anasorb CSC	Methylene chloride/ Methanol (95:5)	1	99.9 (36–225)	82.6
1403 Original	Packed	Anasorb CSC	Methylene chloride/ Methanol (95:5)	10–20	99 (1000–5000)	ND

[A] All Stabilwax and Rtx columns are products of Restek.
[B] All sorbents were obtained from SKC, Inc.
[C] Methyl ethyl ketone (MEK) was previously a single analyte method (NMAM 2500).
[D] Method calls for a beaded carbon tube: Anasorb 747 (SKC 226-81), Anasorb CMS (SKC 226-121), Carboxen-564 (Supelco ORBO 90), or equivalent.
[E] Desorption efficiency and stability studies were conducted using Ambersorb XE-347 tubes (equivalent to a current Anasorb 747 tube).
[F] Recovery was 90% after 6 weeks at 25°C.

on XAD-4 sorbent tubes (SKC, Inc.), desorbed with 1 mL of diethyl ether, and analyzed on a 30-m Stabilwax-DA fused silica capillary column. The LOD was improved to 1 μg/sample as compared with 20 μg/sample as reported in the original method. Improvement in the DE recovery was achieved with the new method: an average of 94.1% over the range of 55 μg to 831 μg compared with only 86% over a range of 849 μg to 3400 μg in the original packed column method. A 30-day storage stability study was completed in the new method with a recovery of 82.4%. No 30-day storage stability results were reported in the original method.

TABLE III. Comparison of New and Previous Phase 3 Methods

Analyte (NMAM Method No.)	Column[A]	Sorbent[B]	Solvent	LOD (μg/sample)	DE (%) (range studied in μg/sample)	30-Day Storage Stability Study (%)
Methyl acrylate						
2552 New	Rtx-35 (30 m)	Anasorb CMS	Carbon disulfide	0.5	92.3 (19–172)	105.3
1459 Original	Packed	Anasorb CSC	Carbon disulfide	10	81.2 (87–350)	ND
Methyl methacrylate						
2537 New	Rtx-35 (30 m)	XAD-2	Carbon disulfide	0.4	100.4 (16–283)	96.2
2537 Original	DB-1[C] (30 m)	XAD-2	Carbon disulfide	10	96 (560–2400)	97.3
Ethyl methacrylate[D]						
2537 New	Rtx-35 (30 m)	XAD-2	Carbon disulfide	0.5	102.3 (15–275)	99.8
2-Heptanone						
2553 New	Rtx-200 (30 m)	Anasorb CMS	Carbon disulfide/ Isopropanol (98:2)	0.5	97 (40–1205)	99.4
1301 Original	Packed	Anasorb CSC	Carbon disulfide/ Methanol (99:1)	50	82 (500–10,000)	ND
3-Heptanone						
2553 New	Rtx-200 (30 m)	Anasorb CMS	Carbon disulfide/ Isopropanol (98:2)	0.7	100.4 (20–603)	98.4
1301 Original	Packed	Anasorb CSC	Carbon disulfide/ Methanol (99:1)	50	94 (250–7000)	ND
5-Methyl-3-Heptanone						
2553 New	Rtx-200 (30 m)	Anasorb CMS	Carbon disulfide/ Isopropanol (98:2)	0.7	98.7 (11–330)	99.0
1301 Original	Packed	Anasorb CSC	Carbon disulfide/ Methanol (99:1)	50	90 (150–4000)	ND
Mesityl oxide						
2553 New	Rtx-200 (30 m)	Anasorb CMS	Carbon disulfide/ Isopropanol (98:2)	0.3	95.0 (9–275)	99.3
1301 Original	Packed	Anasorb CSC	Carbon disulfide/ Methanol (99:1)	50	81 (100–3000)	ND
Camphor						
2553 New	Rtx-200 (30 m)	Anasorb CMS	Carbon disulfide/ Isopropanol (98:2)	0.7	97.0 (9–302)	93.9
1301 Original	Packed	Anasorb CSC	Carbon disulfide/ Methanol (99:1)	50	97 (20–400)	ND

[A] All Rtx columns are products of Restek.
[B] All sorbents were obtained from SKC, Inc.
[C] Column is a product of J&W Scientific, Inc. (Folsom, Calif.).
[D] No official previous method for ethyl methacrylate exists. Previously, NMAM 2537 was a single analyte method for methyl methacrylate.

The second method evaluated was NMAM 1460 (Isopropyl Acetate). In both the new and original methods, isopropyl acetate is collected on coconut shell charcoal sorbent tubes. However, in the new method, the desorption solvent was changed to carbon disulfide/methanol (99:1). An improvement in the DE recovery was achieved: 98.4% over the range of 17 μg to 698 μg when compared with a recovery of 86.2% over the range of 3750 μg to 15,400 μg reported in the original method. The use of an Rtx-1 fused silica capillary column (Restek) allowed the LOD to be lowered to 0.2 μg/sample in the new method versus 10 μg/sample in the original packed column method. A 30-day storage stability study was completed (99.9%), whereas no storage stability results were reported in the original method.

The final method evaluated was NMAM 1618 (Isopropyl Ether). In both the new and original methods, isopropyl ether was collected on coconut shell charcoal and desorbed with 1 mL of carbon disulfide. In the new method, the LOD was lowered to 0.2 μg/sample as compared with 10 μg/sample in the original packed column method. An improvement in the DE recovery at lower levels was achieved (100.9% over the range of 11 μg to 651 μg as compared with an average of 94% over the range of 3160 μg to 12,580 μg). A 30-day storage stability study was completed in the new method (98.2%), whereas no 30-day storage stability results were reported in the original method.

CONCLUSION

The methods described and evaluated in this project have incorporated the most recently available fused silica capillary column technology. Through the selection of alternative desorption solvents and improved or new solid sorbent media, combined with the improved resolution afforded by capillary column chromatography, the desorption efficiencies were improved for each analyte even when evaluated at substantially lower concentrations (approximately 5–10× LOQ to 0.1× REL/PEL). Capillary columns, coupled with more sensitive gas chromatographs and data collection systems, resulted in lower LOD values by a factor of ten- to twentyfold for most analytes evaluated. Thirty-day storage stability studies, generally not performed in the original packed column methods, were successfully completed to meet current method development criteria.

Finally, an additional benefit includes the combination of several single analyte methods into chemically analogous multianalyte methods. For example, trichloroethylene (previously NMAM 1022) was incorporated into the Halogenated Hydrocarbons method (NMAM 1003) and methyl ethyl ketone (previously NMAM 2500) was incorporated into the Ketones I method (NMAM 2555) because of the selection and use of a different sampling media that was chemically inert to the highly reactive analyte MEK. Furthermore, several analyte isomers were incorporated in some methods because of the improved separation afforded by capillary column chromatography. Examples include the addition of o-, m-, and p-xylene and β-methylstyrene to the Aromatic Hydrocarbons method (NMAM 1501). Additionally, this research provided evidence that some analytes did not meet the current method development criteria, such as naphthalene, which was dropped from the Aromatic Hydrocarbons method because it failed to meet the current recovery criteria for DE and storage stability during the method development evaluation.

Thus, it can be concluded that the methods discussed in this manuscript have successfully addressed the problems and concerns identified in the NMAM client survey. The methods developed as part of this research will equip occupational and environmental hygienists with new and/or improved procedures for the sampling of environmental and workplace chemical hazards. The analysis of field samples in the laboratory will be conducted with methods developed using the most technologically modern gas chromatography techniques, resulting in lower detection limits and improved sample recoveries. Furthermore, these new or revised methods are also suitable for application to the sampling and analysis of any chemicals present at the site of a chemical terrorism incident.

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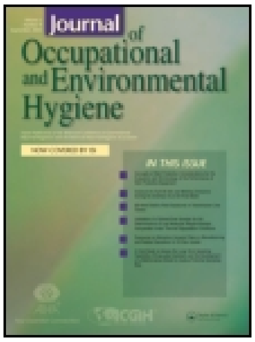

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