Quantitation of Trimethyl Amine by Headspace Gas Chromatography–Mass Spectrometry Using a Base-Modified Column

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Abstract

Headspace gas chromatography–mass spectrometry (GC–MS) has been successfully applied to the analysis of the highly volatile species trimethyl amine (TMA). TMA quantitation in fiberglass insulation resins (ultimately used by the automotive and building products industries) is of interest because of its highly odoriferous nature. The release of TMA from fiberglass insulation products is the principal component responsible for the "fishy" odor encountered in automobiles. Currently, the industry standard for the analysis of TMA involves injecting an aqueous insulation extract into the GC–MS equipped with a polyethylene glycol column. Several problems inherent in this analysis prohibit consistent performance and enhance the possibility for wide variations in the quantitative results. This article reports the development of a new approach to the quantitation of TMA from fiberglass insulation between the levels of 1 and 150 ppm.

Introduction

For several years, the automotive industry has been engaged in efforts to reduce the release of volatile organic compounds (VOCs) from their products. These releases are manifested in many ways, both positive and negative. One of the positive manifestations is the familiar "new car smell" and is attributed to the complex emissions of several components of materials used in the cab interior (1). One of the more negative manifestations encountered occurs as the vehicle ages and results in the "fishy" odor that slowly intensifies and permeates the headliner and the hoodliner areas. This odor has been attributed to the evolution of trimethyl amine (TMA) (2,3) and is a result of the continuous contact in moist air of byproducts formed during the curing of the insulation binder. The formation of TMA is a result of the reaction of formaldehyde with ammonia, ammonium salt, or an amide-containing compound (shown in Figure 1), and its persistence continues after the initial condensation of the resin and remains as long as there is an imine-forming moiety available (4). An accepted mechanism is shown in Figure 2 (5). In a recent study by S. Sato et al. (6) at Toyota Central Laboratories (Aichi, Japan), it was found that the release of TMA in 17 new model cars causes TMA concentration levels ranging from undetectable to 14 ppb. This level exceeds the olfactory threshold level (OTL) by approximately 6 times (OTL for TMA = 2.4 ppb). Furthermore, the analysis of residual nitrogen has suggested that the evolution of the low-molecular-weight trialkyl amines will continue until they are almost completely exhausted from thermosetting resole resins (7).

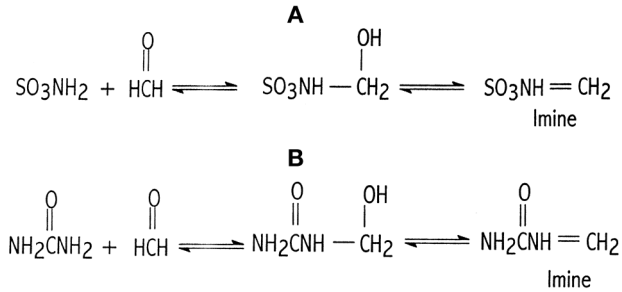

Figure 1. Reaction between (A) sulfamic acid and formaldehyde and between (B) urea and formaldehyde.

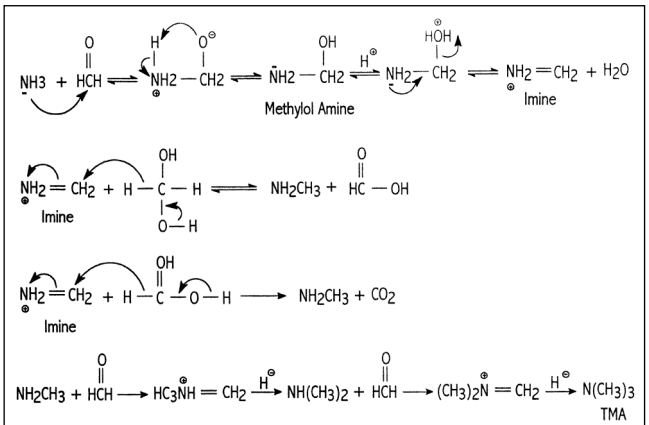

Figure 2. Suggested mechanism for the formation of TMA.

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Fiberglass insulation products are used in a wide range of both consumer and industrial applications outside the automotive industry. They include office building room dividers; metal building insulation; air-handling systems; and residential building insulation batts, blankets, and blowing wool.

Some of these fiberglass insulation products (such as metal building insulation and residential insulation) have general odor specifications that state that the product must have no objectionable odor (8). Other products, such as automotive headliners and hood liners have specific TMA requirements to ensure that a given product releases less than a specified amount of TMA as determined by using the industry-accepted standard technique for measuring TMA.

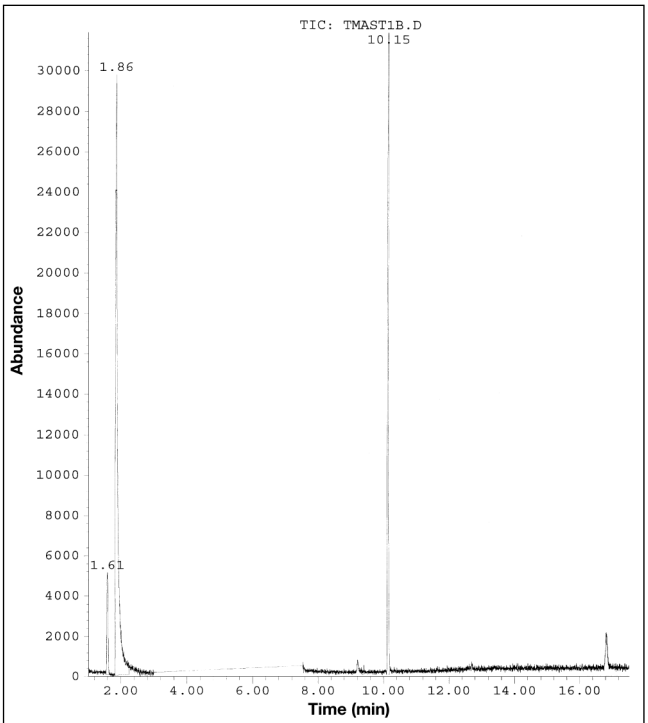

Figure 3. Expected TIC response for liquid sample injection on a properly operating instrument (ion abundance versus time in minutes).

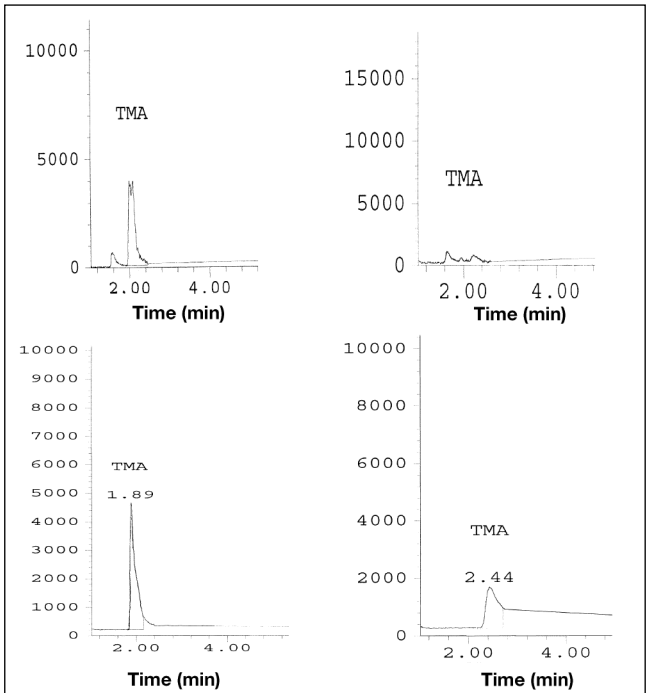

Figure 4. Typical peak shape variations of TMA using a liquid injection technique. (ion abundance versus time in minutes).

Insulation manufacturers prepare these products by spraying urea or melamine-modified phenol–formaldehyde resin onto the glass fibers; then, they cure them at a high temperature in either an oven or a press depending on the application. During curing, TMA forms from the reaction between formaldehyde and nitrogen components of the binder (9). After curing, the product becomes susceptible to TMA volatilization when exposed to conditions of high heat and humidity. Under these conditions, moisture contacts the glass, leaching alkalinity out of the glass. When this alkaline moisture contacts the TMA in the binder, TMA volatilizes, causing the objectionable fishy odor.

Currently, the most commonly used method for the quantitation of TMA is that method developed for the automotive industry (10). This method used the available technology of the time to yield a reasonable result for a reasonable cost. Quantitating TMA involved injecting the aqueous extract of an insulation mat into a gas chromatograph and a packed or capillary column and employing a flame ionization detector to avoid interference with water. Although this technique works well for most volatile and semivolatile analyses, it suffers from several fundamental chromatographic effects that cause severe precision and accuracy issues when analyzing for an amine, especially when that compound is a gas at room temperature (11). Occasionally, the TMA response was acceptable (shown in Figure 3), but more typically the analysis yielded poorly shaped peaks such as those shown in Figure 4 and statistically demonstrated in Table I. As Table I indicates, the variability of the response of TMA (as measured using the "industry standard" analysis) prohibited quantitation with reasonable precision. Inquiry into the quantitative procedure at several manufacturers of fiberglass insulation made it clear that the problems encountered with this method were universal when performing the method as defined by the automotive industry. Thus, the principle drive for developing a more accurate and precise quantitative method was to correct the previously mentioned inconsistencies.

Experimental

The following describes the method used for preparing the fiberglass insulation material and collecting the TMA from the insulation for testing in this experiment.

The fiberglass insulation material used in these experiments was made by bonding fiberglass with a phenolic insulation binder. The binder was prepared from phenolic resin containing unreacted formaldehyde, urea, water, and ammonium sulfate. In the two-step process, the phenolic–formaldehyde resin was initially reacted with urea to minimize any free formaldehyde. This "prereaction" was completed after 16 h. Step 2 was the reaction between the mix of step 1, water, and the latent acid catalyst ammonium sulfate. Because the binder had a limited shelf life, it

was used within 12 h.

One-inch-thick unbonded fiberglass batts were impregnated with the binder by atomizing the binder and drawing it through the batt so that the resulting loss on ignition (LOI) was between 5% and 10%. The LOI was estimated by weighing the batts before binder application and then reweighing them after being cured. The prepared batts were cured in a press that was placed inside an AA Aalberg oven at 525°C for 1 min.

After curing the batts, the General Motors' TMA test method was used to extract the TMA from the fiberglass batt. The batts were cut into one-inch cubes. Ten milliliters of distilled water was weighed into 1-quart glass jars. A 6.5-cm-tall sample support was placed in the jar. Twelve grams of insulation cubes was weighed to the nearest 0.1 g onto a piece of cheesecloth. The cheesecloth was wrapped loosely around the insulation cubes and placed on top of the sample support. The lid was placed on the jar and screwed on firmly to prevent water from evaporating. The jars were placed in an oven at 65°C for 16 h. The jars were removed from the oven and allowed to cool to room temperature for 30 min. The insulation and the sample support were removed from the jar and the water was transferred to a scintillation vial. Samples were prepared for TMA analytical testing by pipetting into a 22.00-mL headspace (HS) vial, 1.0 mL of the aqueous extract from the scintillation vial, and 1.0 mL of a 0.01N sodium hydroxide solution containing a known quantity of *n*-octanol as an internal standard. Samples were then analyzed by HS-gas chromatography (GC)–mass spectrometry (MS).

A Hewlett-Packard (Palo Alto, CA) 5971A GC–MS with a Tekmar (Cincinnati, OH) 7000 HS autosampler input was used to acquire the reported data. A temperature equilibration time of 20 min per sample was used at each analysis temperature. The vial pressure was approximately 20 kPa above the ambient pressure at the analysis temperature of 95°C. Valve and transfer line temperatures were held at 135°C and 140°C, respectively, and the helium carrier gas sweeping the sample into the GC was 40 mL/min. The HS gas injection volume was 1.0 mL.

Table I. Variability of the TMA Standards' Peak Area Representative of the Peaks Shown in Figure 2

Compound	Figure 2A %RSD	Figure 2B %RSD	Figure 2C %RSD	Figure 2D %RSD
TMA	55.8	130.4	10.5	37.1
Internal standard	56.0	45.6	10.5	31.1
Response factor	0.7	100.7	0.0	7.4

Table II. FET Calibration Curve Data*

Compound	Level 1	Level 2	Level 3	Level 4	Calibration check 1	Calibration check 2
TMA	2.6	26	52	104	22	34
Internal standard	72	72	72	72		
Measured					24	33

* Reported quantities listed are micrograms per milliliter in matrix prior to partitioning $[A]_o$.

The chromatographic separations were performed using a 30-m × 0.25-mm-i.d. HP Basic Wax column having a 0.5-µm film thickness. The temperature program consisted of an initial oven temperature of 40°C held for 4 min, during which time the TMA eluted. After the 4-min hold, the temperature was ramped at 35°C/min to 150°C and then ramped at 10°C/min to 190°C with a final hold time of 2.0 min, during which time the internal standard eluted. Nominally, the internal standard elutes at 10.7 min. The choice of internal standard will be discussed. A constant carrier gas flow was employed and held at 0.50 mL/min (25.1 cm/s). No data was collected from 3.6 to 9 min in order to avoid filament damage during the elution of the aqueous matrix and minimize data file size.

Data acquisition was via a secondary ion monitoring experiment (SIM). For the identification and quantitation of TMA, ions 42, 58, and 59 were monitored with quantitation based on the response of ion 58, and identification was based on the ratio of ions 58 and 59 at approximately 1:0.5. Ions 41, 56, 70, and 84 were used to identify the internal standard (*n*-octanol), and the response of ion 56 was used to determine the response factor. It should be noted that triethyl amine (TEA) can also be detected in this SIM experiment because of the 58- and 59-amu fragments in its mass spectrum. However, the chromatographic conditions should facilitate approximately a 1-min separation in the retention time (t_R), and the typical ion ratio of the 58:59 ratio of TEA fragments should be on the order of 1:0.1.

The calibration curves used in this study were constructed by averaging the response of three replicate injections of four levels of a modified full evaporative technique (FET) standard (Table II). The modifications to the FET method will be discussed.

The standards can be prepared from either a TMA solution available from Aldrich Chemicals (Cat. # 42,647-4) (25–27% TMA solution by weight in water) that will require standardization prior to use or from the trimethylammonium chloride salt, also available from Aldrich (Cat. # T7,276-1, 98%). A 2500-µg/mL stock solution was prepared from the purchased reagents by weight (if using the hydrochloride salt) or by volumetric dilution (if using the 25–27% solution). When preparing the stock solution using the salt, it was necessary to adjust the weighed quantity of salt to account for the quantity of TMA in the salt by multiplying the weighed amount by 0.618. When preparing the stock solution using the TMA solution, it was necessary to first standardize the purchased TMA solution. Standardization consisted of a back titration of the solution with a known concentration of a HCl solution using phenolphthalein as an indicator. Our laboratory predominately uses the 25–27% solution because the standardization is reasonably simple to complete and refrigerated storage is readily available. However, care must be used to prevent excessive loss of TMA from the solution when making the analytical standard. It should be noted that the chloride salt is highly hygroscopic and must be stored properly. Rapid degradation of the standard will occur if the standard is left open to the environment.

The extraction solvent used in the experiment consisted of a known quantity of *n*-octanol dissolved into a 0.01N sodium hydroxide solution. The solvent was prepared by heating approximately 150 mL of pure water to approximately 75°C and adding it to a 250-mL volumetric flask containing an accurately weighed quantity of *n*-octanol. The flask was capped, shaken occasionally

to promote the dissolution of the octanol, and allowed to come to room temperature. Twenty-five milliliters of 0.1N NaOH was added to the volumetric flask, and pure water was added to the mark. The flask was allowed to set for an additional 30 min, and the volume was checked for accuracy. The typical concentration of the octanol internal standard was approximately 50 µg/mL.

From the stock standard solution, volumetrically diluted standards were prepared. In order to prepare the HS standard, 1.0 mL of pure water (Fisher Scientific) (Cat. # W5-1, HPLC-grade water) was pipetted into each standard vial and followed by pipetting 1.0 mL of each level of prepared TMA standard. The 2-mL total matrix volume duplicated the 2-mL sample–internal standard matrix volume. Data were collected from 1.8 to 14 min. The 1.8-min delay was used to avoid acquiring data during the air peak elution occurring at 1.6 min after injection. Void volume was noted at approximately 1.5 min. The relative standard deviation (RSD) of the data for each standard level (three replicates per level) was less than 4.0% in all cases except the lowest level.

Results and Discussion

The compounds of interest (displayed in Figure 5) eluted as TMA (t_R = 2.3 min) and the internal standard *n*-octanol (t_R = 10.7 min). Relative to the peaks formed using the original method (which are exhibited in Figures 3 and 4) the new method yielded a more symmetrically eluted TMA (inset in Figure 5), demonstrating far fewer column/analyte interactions than experienced under the conditions of the original method.

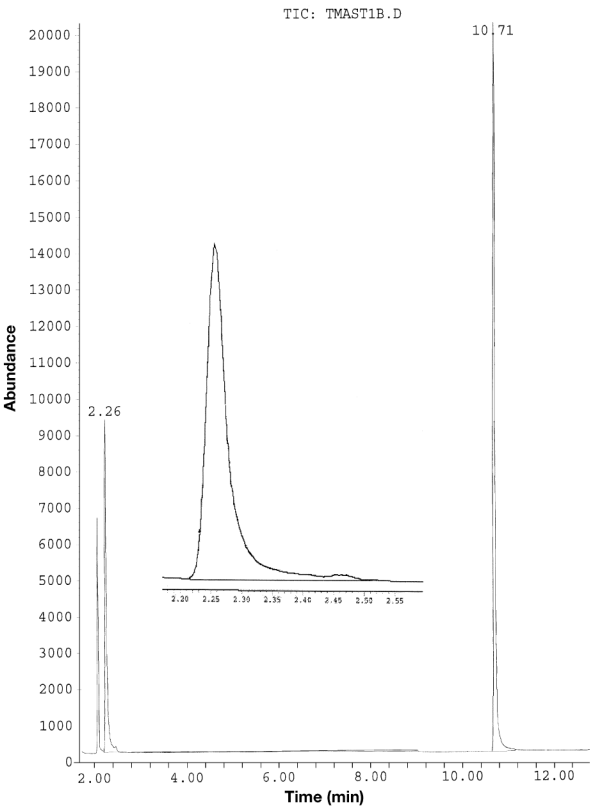

Figure 5. TIC of a TMA standard using HS sampling and a base-modified GC column. The sample was at T = 95°C. The inset shows an expanded TMA peak.

As stated previously, the goals of the project were to eliminate the large variability in reported quantities of TMA, improve the peak shape, and reduce or eliminate the high degree of column/analyte interaction. Because the aqueous extraction of the insulation product was ancillary to the anomalies of the quantitation and used throughout the automobile and insulation industries, it was anticipated that there would be resistance to changing that part of the experiment. Therefore, the analytical sample introduction technique, chromatography, and data acquisition had to be independent of the initial extraction, but remain compatible with the insulation sample preparation. In other words, the sample to be quantitated would consist of an aqueous extract of a weighed glass insulation composite.

In the original method, the chromatographic conditions (such as column temperature, flow rate, and injection port temperature) were chosen in order to increase the t_R of TMA on the column. The end result was that TMA retention could be extended to approximately 4.5 min, but it still suffered from the typically poor peak shape encountered with many primary and secondary amines and the peak area variation was only marginally improved. Changing to a nonpolar polydimethyl siloxane column or to a diphenyl dimethylsiloxane copolymer column resulted in no significant improvements. The installation of a base-modified polyethylene glycol column virtually eliminated the peak tailing associated with the standard polyethylene glycol column used previously. The change to a base-modified column also resulted in an increase in signal-to-noise that was greater than expected, indicating that the TMA interactions with the unmodified polyethylene glycol extended well-beyond the observable peak width. However, even with the base-modified column the variation in the peak area and shifts in t_R persisted.

It was suspected that part of the variability in the peak area of TMA was caused by the turbulent conditions encountered in the injection port. This contention was supported when reduced peak variation was observed in TMA samples of 300 ppm or greater and a split injection was used. The split injection greatly reduced sensitivity and was abandoned as a suitable part of the method. In order to increase sensitivity, the split/vent valve time was increased to 1.0 min. This resulted in a significant reduction in the peak variation and an increase in the peak area. However, it also resulted in an extraordinary widening of the peak base line and a return to a significant tailing problem that negated any advantage of peak area increase. The result was an overall reduced sensitivity unsuitable for the quantitation of TMA in samples containing less than 100 ppm.

HS sampling eliminated these problems (including the turbulence in the injection port caused by the sample introduction) and it accomplished several other important objectives. It allowed approximately a 45-fold increase of sample size into the GC. It reduced the rate of column degradation by limiting the quantity of semivolatile components being placed onto the column. Finally, it either eliminated or greatly reduced matrix interferences associated with the liquid phase. In order to take advantage of the high volatility of TMA and the large difference in the boiling points between TMA and the water matrix, 95°C was chosen as the equilibration temperature. At the HS equilibration temperature of 95°C and with a minimum matrix volume, the TMA can be

considered to be fully evaporated. At 95°C, the quantitation of TMA can be accomplished in the usual manner for HS quantitation (12) because the analysis temperature is approximately 30 times the boiling point of TMA. However, to account for possible organic interferences and variations in the instrument and samples, an internal standard technique for quantitation was preferred. *n*-Octanol was selected because it eluted late in the chromatogram, which removed it from any interference from the water matrix. Lower-molecular-weight alcohols such as ethanol, propanol, and butanol were candidates for the internal standard, but their use was prohibited by interferences from the aqueous matrix. In a typical HS experiment, the internal standard is chosen such that it will be fully evaporated at the analysis temperature (in this case 95°C). In this application, however, it must be noted that at 95°C the internal standard was partitioning between phases according to its environment and chemical potential because the boiling point of *n*-octanol is 196°C. At 95°C, *n*-octanol was preferentially in the aqueous phase owing to its low volatility and its ability to hydrogen bond. Despite this, *n*-octanol was an effective internal standard because its poor solubility in water promotes *n*-octanol into the gaseous phase. Another factor impacting *n*-octanol's volatilization is the matrix volume. Because changes in the matrix volume will affect the detected peak area of the internal standard (and also the response of TMA), it was imperative to choose a suitable matrix volume and fix the volume of all subsequent samples in order to achieve a precise and accurate response factor and thus quantitation of TMA. In a typical HS quantitation, it is imperative to know the matrix volume (13,14); therefore, the careful application of the sample in this method was an expected qualification.

Also in this method, it was necessary to limit the matrix volume to accommodate the limited volume of insulation extract. A volume of 2 mL or less was chosen. By fixing the total volume of the standards and samples, the partition coefficient for both compounds can be neglected. Table III shows the dependency of the two compounds' peak response on the matrix volume. As the matrix volume is increased while maintaining a constant analyte mass (or a reduction in the original analyte concentration in the matrix), the response of both the TMA and the octanol decreases as expected. However, from 1 to 2 mL there was very little change in the response of the TMA signal. This can be considered to be representative of a fully evaporated compound. In the second part of that experiment (lower half of the table) the concentration of the TMA and the internal standard were maintained at 22.5 and 72 ppm, respectively. As the table shows, the response increased with volume and should ultimately result in a more sensitive quantitation. However, sample size restrictions and other economic considerations currently prohibit this approach.

Figure 6 demonstrates the linearity of the method in solutions representative of samples containing from 2 to 104 ppm of TMA. With an average correlation coefficient of 0.999, it is evident that the method was linear to less than 3 ppm. However, the %RSD of the lowest level exceeded 15%, indicating that the method was close to its limit of quantitation. The quantity of TMA injected into the GC–MS at the low-level standard was 0.118 µg/mL (118 ppb) in the HS (equivalent to the response of a water sample containing 2.6 ppm). Calibration data collected on standard solutions from 19 to 152 ppm exhibited comparable linearity data (i.e., cor-

Table III. ISTD* Peak Response Dependency on Sample Volume

Matrix (mL)	Ratio (V_g/V_m)	$[TMA]_o$	TMA response at 95°C	$[ISTD]_o$	ISTD response at 95°C
1	21.00	19.00	13874	72	27133
2	10.00	9.50	13129	36	18964
4	4.50	4.75	8568	18	11913
6	2.67	3.17	6147	12	8193
1	21.00	22.50	19707	72	25345
2	10.00	22.50	30993	72	34272
4	4.50	22.50	40138	72	40527
6	2.67	22.50	44452	72	42887

* ISTD, internal standard.

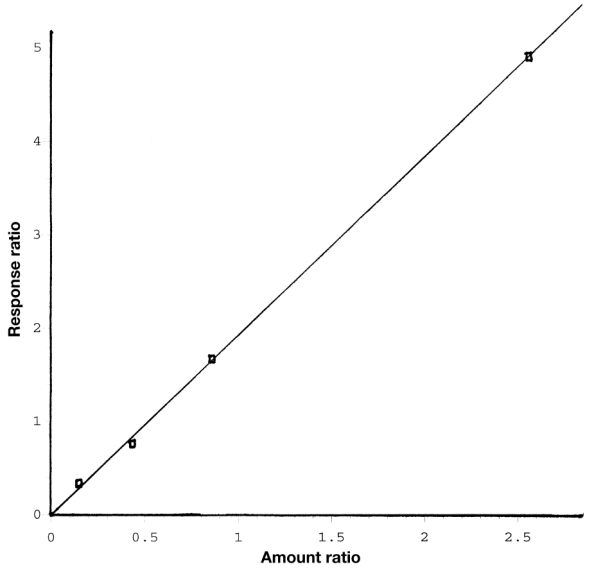

Figure 6. TMA calibration curve with standards from 2.6 to 104 ppm. The correlation coefficient was 0.999, the response ratio 1.92 times the amount, and the curve fit was linear per (0,0).

Table IV. %Recovery of Eight Spiked "Real World" Samples

Sample	Measured TMA	Measured TMA spiked	Spike amount	%Recovery
Binder A	29	59	33	90.0
Binder B	21	51	33	90.0
Binder C	7	42	33	104.9
Binder D	14	47	33	99.0
Binder E	17	50	33	99.0
Binder F	35	68	33	99.0
Binder G	15	46	33	93.0
Binder H	11	42	33	93.0
Average %recovery				**96.0**

relation coefficients of 0.998 or better).

Table IV demonstrates the results of a recovery percentage study in which 8 samples with TMA quantities measuring from 7 to 35 ppm were spiked with 33 ppm of TMA. The spiked samples were prepared and analyzed simultaneously with their unspiked complements. As Table IV shows, the HS technique yielded a very effective means of extraction at the 95°C equilibrium temperature. The quantitation of TMA from "real world" samples consisting of over 100 extractions over a 4-month period consistently yielded %RSD values of the TMA peak areas of less than 5% and %RSDs of less than 4% on the quantitative result of multiple replicates (three or more samples).

Conclusion

In conclusion, the use of HS sampling coupled with the base-modified polyethylene glycol column has been shown to be a reproducible and accurate technique for the quantitation of TMA. It has also been shown that this method is a reasonable alternative to what is currently being used and does not entail the usual manipulations of data normally associated with HS analysis (i.e., partition coefficients and HS volumes). In addition, the performance of this method can be achieved with relatively inexpensive instrumentation costs and columns commonly available.

Acknowledgments

We would like to acknowledge Dr. David Valdez (Analytical Department Group Leader) and Dr. Kurt Gabrielson (Industrial Resins Group Leader) (Georgia-Pacific Resins, Inc.) for allowing the time to complete this project; Mr. Tom Kergil (Senior Development Chemist) (Georgia-Pacific Resins, Inc.) for his introductory development on this project; and our fellow colleagues, Randy White, Nicole Thompson, Jesse Petrella, Ellen Nagy, Kari Fowler, Jason Rivers, Sean Pegram, and Laura Banister, for their critical suggestions and sample preparations.

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Manuscript accepted April 10, 2002.