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Development and Scale-Up of an Aqueous Ethanolamine Scrubber for Methyl Bromide Removal

Kevin Hettenbach,* David J. am Ende, Kyle Leeman, Eric Dias, Narasimhan Kasthurikrishnan, Steven J. Brenek, and Paul Ahlijanian

Pfizer, Inc., Pfizer Global Research and Development, Chemical Research and Development, Eastern Point Road, Groton, Connecticut 06340, U.S.A.

Abstract:

A scrubber system was developed specifically to remove methyl bromide liberated during a demethylation process. On-line mass spectrometry (MS) was implemented and developed as a tool to monitor and quantify the methyl bromide scrubber efficiency during the demethylation reaction for laboratory and pilot-plant campaign runs. The MS technique is relatively simple to interface to existing equipment, requires no direct sample contact, and allows for the sampling from multiple ports. Results of the MS on-line monitoring using ethanolamine for both the laboratory and pilot plant showed scrubber removal efficiency of >99%. In addition to MS, ion chromatography and other gravimetric methods were implemented to confirm the level of methyl bromide consumed by the scrubber.

1. Introduction

Methyl bromide, produced during certain demethylation reactions, poses environmental and safety concerns and therefore must be controlled upon scale-up. Methyl bromide (MW = 94.94) is a volatile organic compound (VOC) and is a potential occupational carcinogen.[1] The objectives of this work were the following: (1) to develop an effective scrubber system to convert methyl bromide, generated from demethylation reactions (Scheme 1), to a form suitable for liquid waste disposal, (2) to develop mass spectrometry (MS) as a tool to monitor scrubber efficiency, (3) to scale-up and transfer MS into the pilot plant to monitor methyl bromide and to verify scrubber effectiveness, and (4) to ultimately mitigate methyl bromide entry to the environment. For background information and other applications of process MS in the pharmaceutical industry, see refs 2 and 3.

There are only a few papers in the literature on the topic of controlling methyl bromide vapors. In one patent, activated carbon was used to adsorb methyl bromide, followed by desorption and secondary treatment with sodium hydroxide solution (to react with methyl bromide).[4] Disadvantages of this method are the disposal of spent carbon and the need for secondary treatment. In another paper, thermal decomposition using a propane burner showed promise as a viable method to reduce methyl bromide emissions;[5] however, highly acidic hydrogen bromide (HBr) was produced as a reaction byproduct, and therefore secondary treatment is required.

Alkanolamines in the presence or absence of an alkyl metal hydroxide were shown in the literature[6] to be a viable medium for the abatement of methyl bromide waste gas. Advantages of ethanolamine are that it is highly reactive to methyl bromide and acid vapors (i.e., HBr) and the reaction byproducts are soluble in water and suitable for wastewater treatment. The present work extends the applications of ethanolamine to a scrubber system for a pharmaceutical pilot plant.

To ensure that methyl bromide was being consumed by the scrubber, an on-line analytical tool was needed. Mass spectrometry was chosen in the present work because of (1) the ability to multiplex several sampling ports, (2) its high sensitivity, (3) the ability to monitor multiple gases, and (4) the ease at which it can be interfaced to the piping of a scrubber system. Previous work has shown the use of on-line mass spectrometry to monitor compositions in process streams.[7−9] The present work demonstrates for the first time the use of MS to monitor and quantify scrubber efficiency in a pharmaceutical pilot plant.

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* To whom correspondence should be addressed. Pfizer, Inc., Chemical R&D, MS 8156-69, Groton, CT 06340. E-mail: kevin_w_hettenbach@groton.pfizer.com.

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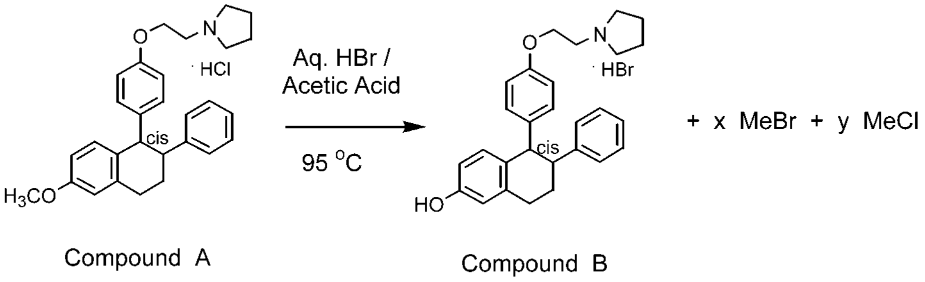
Scheme 1. **Demethylation reaction: compound A, glacial acetic acid, and aqueous hydrobromic acid (48%) are combined in a stirred vessel and heated to 90−95°C until reaction completion is indicated by HPLC (reaction time ≈ 24 h); the reaction liberates primarily methyl bromide during the aqueous hydrobromic acid addition, and a small percentage of methyl chloride and hydrogen chloride are evolved due to the chloride ion present as the HCl salt of the substrate; methyl halide balance: $x + y = 1$ equiv (balance of HCl remains in solution)**



2. Experimental Section

2.1. On-Line Mass Spectrometry Analysis. The instrument used for both laboratory and pilot-plant scrubber analysis was an Ametek/Dycor X-proof, multiport quadrupole mass spectrometer (model: Dycor ProMaxion) with a mass range of 1−300 Da. The Dycor System 2000 software was used in tandem with the ProMaxion software to collect mass spectra and control valve switching between the inlet ports, respectively. The inlet capillary lines were polyetheretherketone (PEEK) tubing 0.030 in. in diameter and 12 ft in length. The capillary was maintained at ambient temperature and was interfaced to vent piping via swagelok fittings. The vacuum pressure inside the mass spectrometer was 5×10^{-6} Torr. The pressure difference between the vent line and the mass spectrometer created the driving force for the introduction of gas sample through the capillary. As a safety precaution, the discharge port of the mass spectrometer was vented to an extraction device.

2.1.a. Laboratory Scrubber Analysis. The dual port process MS was interfaced to both the inlet and outlet of a Pyrex gas washing bottle, thus allowing the detection and analysis of methyl bromide gases (Figure 1). Experiments were conducted by flowing pure methyl bromide into a 500-mL Pyrex gas bottle, containing various ethanolamine (redistilled, 99.5+% (Aldrich)) scrubbing solutions. Matheson flow controllers (model 8280) were used to regulate the flow of methyl bromide into the Pyrex gas bottle. To obtain quantitation, an internal standard of argon (MW = 39.95) was used with a constant flow rate of 10 mL/min through the scrubber. The estimated inlet and outlet flow rates of methyl bromide were determined by way of calibration curves of methyl bromide (*m*/*z* 94) against argon (*m*/*z* 40), and then the respective flow rates were integrated over time to compute the total input and outlet mass. A MS calibration curve of methyl bromide flow versus argon flow is shown in Figure 2. Scrubber efficiencies were calculated by comparing the area under the curve of the flow rates of methyl bromide measured in and out of the scrubber and applying eq 1:

$$\text{scrubber efficiency} = \left(\frac{\text{total flow in} - \text{total flow out}}{\text{total flow in}}\right) \times 100\% \tag{1}$$

Independent verification that methyl bromide was being consumed by the scrubber and to confirm efficiency included (1) ion chromatography and (2) silver nitrate titration to quantify the silver bromide precipitate.

2.1.b. Pilot-Plant Scrubber Analysis. Similar to the laboratory setup, the dual-port process MS was interfaced to both the inlet and outlet of the pilot-plant scrubber, thus allowing the detection and analysis of methyl bromide (*m*/*z* 94), methyl chloride (*m*/*z* 50), and hydrogen chloride (*m*/*z* 36) gases. The configuration is shown in Figure 3. The following procedure was followed for determining flow rates/concentrations for each gas in and out of the scrubber:

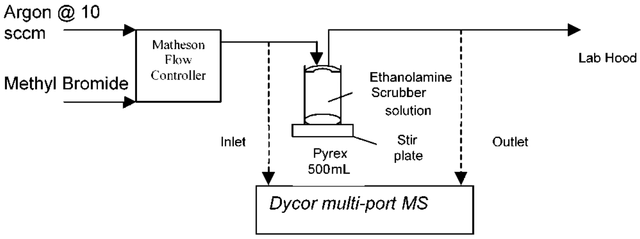


Figure 1. **Controlled flow (Matheson flow controller) of pure methyl bromide and argon (reference gas) into an ethanolamine scrubbing medium (500 mL). The inlet and outlet of the scrubber bottle were monitored for methyl bromide and argon gases using the process mass spectrometer (profile shown in Figure 5). The flow of gas through the capillary is approximately 1 mL/min.**

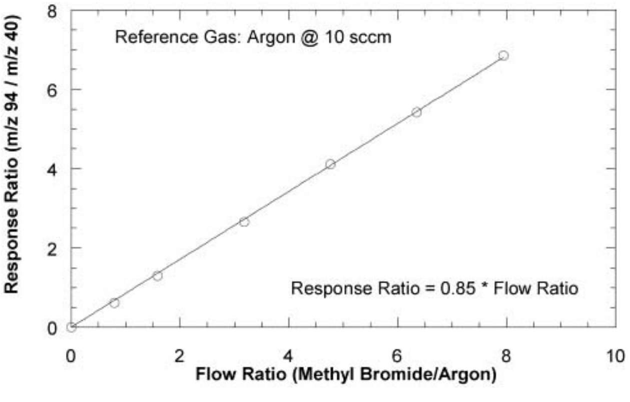


Figure 2. **MS calibration of methyl bromide versus argon. Methyl bromide and argon flows were controlled using a Matheson flow controller. For example, a flow ratio of 2 refers to 20 mL/min of methyl bromide because the argon flow was held constant at 10 mL/min. The *y*-axis is the ion response ratio of methyl bromide (*m*/*z* 94) relative to argon (*m*/*z* 40).**

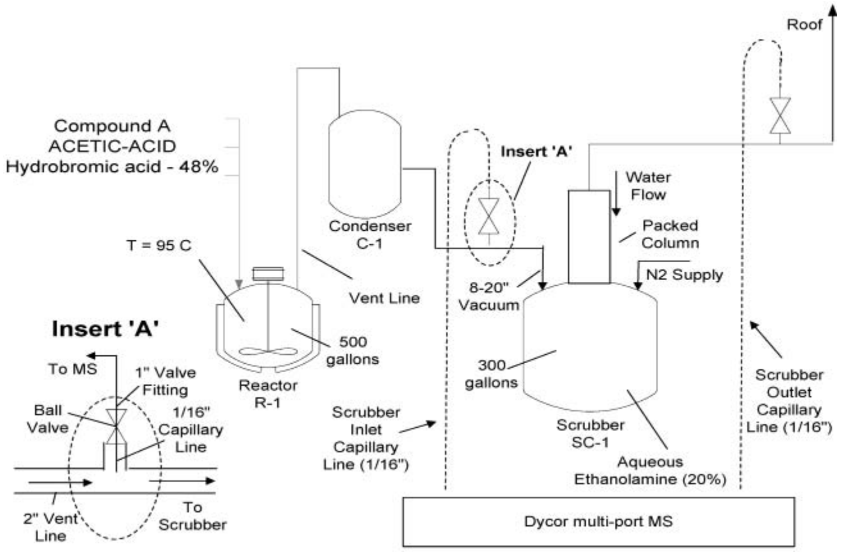


Figure 3. **Pilot-plant equipment configuration for the methyl bromide scrubber system. Methyl bromide vapors evolved upon heat-up of reactor (R-1) to 95 °C, were vented through condenser (C-1) into the venturi scrubber (SC-1). R-1 was under a slight vacuum (8−20 in. H_2O) during the reaction. The Dycor multiport MS was interfaced with the inlet and outlet scrubber vent lines by connecting a 1/16 in. swagelock to a 1 in. valve fitting (Inset A).**

(1) Nitrogen (m/z 28) flow rate was assumed constant and thus was utilized as a reference gas. Note: this is a valid assumption if the scrubber draft pressure is held constant.

(2) Sensitivity factors, calculated by dividing the MS response by the gas concentration, were developed in the laboratory for each gas (eqs 2a−d). Gas concentrations were determined flowing a known amount of nitrogen (N_2), methyl bromide (MeBr), methyl chloride (MeCl), and hydrogen chloride (HCl) using Matheson flow controllers and gas standards. A HCl (1%) in nitrogen standard was used since pure HCl is too corrosive for Matheson flow controllers. Note: every gas introduced into the mass spectrometer will exhibit a different affinity to produce ions (known as ionization probability). When the ionization probabilities of multiple gases are compared to each other, one can calculate the "sensitivity" by dividing the measured amount of gas by its concentration.

$$\text{MeBr SENS} = \frac{m/z\ 94\ \text{A}}{\text{MeBr}\ (\%)} \tag{2a}$$

$$\text{MeCl SENS} = \frac{m/z\ 50\ \text{A}}{\text{MeCl}\ (\%)} \tag{2b}$$

$$\text{HCl SENS} = \frac{m/z\ 36\ \text{A}}{\text{HCl}\ (\%)} \tag{2c}$$

$$\text{N}_2\ \text{SENS} = \frac{m/z\ 28\ \text{A}}{\text{N}_2\ (\%)} \tag{2d}$$

(3) Sensitivity factors were applied to correct individual MS response factors for methyl bromide, methyl chloride, and hydrogen chloride relative to nitrogen (eqs 3a−c).

$$\text{MeBr}_{\text{corrected}} = \left(\frac{\text{N}_2\ \text{SENS}}{\text{MeBr SENS}}\right) \times m/z\ 94\ \text{A} \tag{3a}$$

$$\text{MeCl}_{\text{corrected}} = \left(\frac{\text{N}_2\ \text{SENS}}{\text{MeCl SENS}}\right) \times m/z\ 50\ \text{A} \tag{3b}$$

$$\text{HCl}_{\text{corrected}} = \left(\frac{\text{N}_2\ \text{SENS}}{\text{HCl SENS}}\right) \times m/z\ 36\ \text{A} \tag{3c}$$

(4) The total corrected ion signal (It) was calculated with respect to nitrogen using eq 4.

$$\text{ion total (It)} = \text{MeBr}_{\text{corrected}} + \text{MeCl}_{\text{corrected}} + \text{HCl}_{\text{corrected}} + \text{N}_2\ (m/z\ 28) \tag{4}$$

(5) The individual concentrations were calculated by dividing the individual corrected ion signal by the total corrected ion signal (It), as shown in eqs 5a−d.

$$\text{MeBr}\ (\%) = \left(\frac{\text{MeBr}_{\text{corrected}}}{\text{It}}\right) \times 100\% \tag{5a}$$

$$\text{MeCl}\ (\%) = \left(\frac{\text{MeCl}_{\text{corrected}}}{\text{It}}\right) \times 100\% \tag{5b}$$

$$\text{HCl}\ (\%) = \left(\frac{\text{HCl}_{\text{corrected}}}{\text{It}}\right) \times 100\% \tag{5c}$$

$$\text{N}_2\ (\%) = \left(\frac{m/z\ 28}{\text{It}}\right) \times 100\% \tag{5d}$$

(6) The individual flow rates in and out of the scrubber were calculated by multiplying the total flow by the component concentration (eqs 6a−c). The total flow was calculated by dividing the nitrogen flow by the nitrogen concentration. Note: the nitrogen flow was unknown during the pilot-plant campaign and was estimated by assuming 1 mol of methyl halide is released per mol of compound A (Scheme 1), using an iterative trial and error approach.

$$\text{MeBr flow (L/min)} = \left(\frac{\text{N}_2\ \text{flow (L/min)}}{\text{N}_2\ (\%)}\right) \times \text{MeBr}\ (\%) \tag{6a}$$

$$\text{MeCl flow (L/min)} = \left(\frac{\text{N}_2\ \text{flow (L/min)}}{\text{N}_2\ (\%)}\right) \times \text{MeCl}\ (\%) \tag{6b}$$

$$\text{HCl flow (L/min)} = \left(\frac{\text{N}_2\ \text{flow (L/min)}}{\text{N}_2\ (\%)}\right) \times \text{HCl}\ (\%) \tag{6c}$$

Methyl bromide scrubber efficiencies were calculated by comparing the area under the methyl bromide flow rate curve in and out of the scrubber for the duration of the reaction. Note that *m*/*z* 28, *m*/*z* 36, *m*/*z* 50, and *m*/*z* 94 are parent peaks for nitrogen, hydrogen chloride, methyl chloride, and methyl bromide, respectively. All are unique peaks with the exception of *m*/*z* 36, which includes both hydrogen chloride and methyl chloride mass fragments. In this case, the HCl contribution to *m*/*z* 36 was determined by subtracting the contribution from methyl chloride (e.g., by applying a *m*/*z* 36 to *m*/*z* 50 ratio for methyl chloride, equal to approximately 0.013).

2.2. Ion Chromatography Analysis. Ion chromatography was used to independently confirm and quantify the byproducts of the scrubber. Specifically, this off-line method was incorporated to obtain quantitative results for residual 2-(methylamino)ethanol, dimethylethanolamine, and associated salts that are produced when methyl bromide comes into contact with aqueous ethanolamine (20%) scrubber solutions. Samples were assayed using a standard HPLC (HP1100) connected to an external Waters conductivity detector (model 432). The mobile phase consisted of 0.005% HNO_3 and 0.005 mM EDTA tetrasodium salt dihydrate in H_2O. A Waters cation column; 4.6 × 150 mm × 5 um, was used for the separation. Samples were evaluated versus prepared standards of 2-(methylamino)ethanol and dimethylethanolamine obtained from Aldrich.

3. Results and Discussion

3.1. Demethylation Reaction. The demethylation reaction monitored in the laboratory and pilot plant is shown in Scheme 1. The reaction liberates primarily methyl bromide during the aqueous hydrobromic acid addition, and a small percentage of methyl chloride and hydrogen chloride are evolved due to the chloride ion present as the HCl salt of the substrate. Laboratory analysis of the demethylation reaction indicates that product formation (measured by HPLC) correlates with the methyl bromide offgas profile (i.e., when methyl bromide offgas profile reaches baseline, reaction is complete). The reaction completion time during these studies was shown to be 12−15 h and was shown to follow first-order rate kinetics (Figure 4). The offgas monitoring showed that methyl bromide was liberated to the extent of 0.9 mol/mol of substrate and that small amounts of methyl chloride and HCl were also evolved. The headspace during the demethylation reaction was 500 mL (based on a 1-L vessel), which explains the slower (as measured) evolution of methyl bromide gas before it reaches baseline (i.e., all the methyl bromide must diffuse out of headspace before no MS signal was detected by GC/MS). On-line mass spectrometry could potentially be used as an indicator for reaction endpoint, which could significantly reduce reaction time upon scale-up. Originally in situ FTIR was employed but the highly corrosive nature of the hot HBr/acetic acid caused pitting of the hastelloy probes and thus was abandoned.

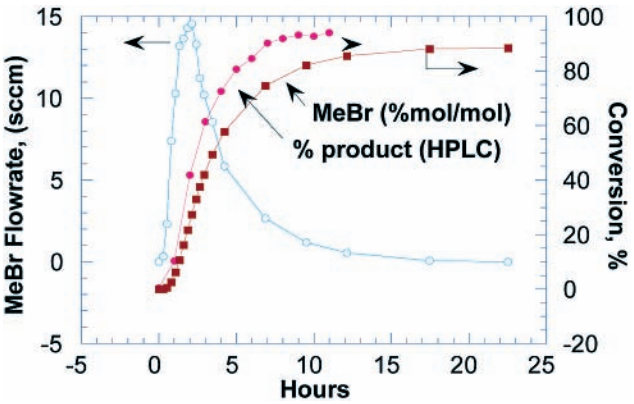
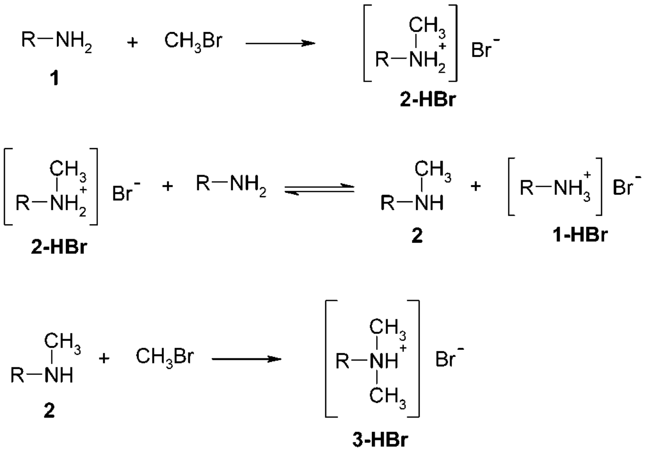


Figure 4. **Correlation of product formation with methyl bromide liberation during the demethylation reaction. The reaction follows first-order reaction rate kinetics. Product formation was measured by HPLC, and the methyl bromide offgas profile was measured using a Hewlett-Packard 6890 GC/MS. The reaction was performed in a 1-L RC-1 vessel, adding 83.2 g of compound A, 218 g of acetic acid, and 305 g of hydrobromic acid (48%), with an approximate headspace of 500 mL.**

Scheme 2. **Reaction mechanism of methyl bromide with ethanolamine, and the formation of monomethylated (2-(methylamino)ethanol) and dimethylated (dimethylethanolamine) byproducts**



3.2. Development of A Methyl Bromide Scrubber System (Laboratory). *3.2.a. Reaction Mechanism of Aqueous Ethanolamine with Methyl Bromide.* The first step in the mechanism of ethanolamine **1** with methyl bromide is to form the 2-(methylamino)ethanol·HBr salt **2-HBr** (Scheme 2). Because of the excess ethanolamine in solution, however, **2-HBr** is in equilibrium with the 2-(methylamino)ethanol free base **2** and the ethanolamine·HBr salt **1-HBr**. Subsequent reaction of **2** with another equivalent of methyl bromide then forms the dimethylethanolamine·HBr salt **3-HBr**, which is also expected to be in equilibrium with its corresponding free base **3** and **1-HBr** (not shown). As a result, for each equivalent of **3-HBr** that is formed, one equivalent of **1-HBr** *must* also be present.

Methyl chloride offgas was detected during MS monitoring of the pilot-plant reaction. The reaction of ethanolamine with methyl chloride follows Scheme 2, with the exception that the HBr salt is replaced with the HCl salt.

3.2.b. Methyl Bromide Scrubber Analysis using On-Line MS. Several ethanolamine scrubber systems were tested in the laboratory using the dual port Dycor MS (Figure 1). The scrubbing scenarios analyzed included: (1) aqueous etha-

Table 1. **Results of Pure Methyl Bromide Scrubbing Experiments**[a]

scrubbing medium	ethanolamine equiv[b]	methyl bromide flow rate (mL/min)	scrubber additions	removal efficiency (%)[d]
aqueous ethanolamine (20%)	3.2	58.3	ethanolamine (84.2 g) water (337 g)	99.1
ethanolamine 20%), methanol (60%), water (20%)[c]	3.2	58.3	ethanolamine (84.2 g) methanol (253 g) water (84.2 g)	99.5
ethanolamine	9.6	87.5	ethanolamine (379 g)	99.9
water	NA	58.3	water (400 g)	0.0

[a] Note: All experiments were run at ambient temperature (22 °C), MeBr input time = 166 min. [b] Based on the amount of methyl bromide added. [c] Water and methanol are miscible in ethanolamine. [d] Removal efficiency was calculated by comparing the area under the curve of the methyl bromide flow rates in and out of the scrubber. Efficiency = ((in − out)/in) × 100%.

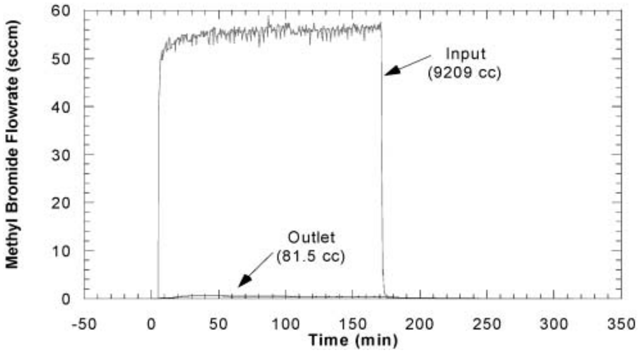


Figure 5. **Results of bubbling pure methyl bromide at a flow rate of 58 mL/min into a solution containing 420 mL of aqueous ethanolamine (20%), see Figure 1 for setup. Methyl bromide flow rates (inlet and outlet) were calculated on the basis of a MS calibration curve versus argon. Scrubbing efficiency = ((9209 mL − 81.5 mL)/9209 mL) × 100% = 99.1%.**

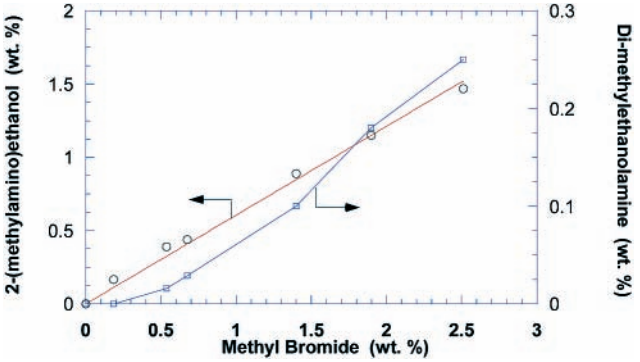


Figure 6. ***x*-axis is the wt % of methyl bromide in aqueous ethanolamine (20%) as prepared gravimetrically. The *y*-axes are the wt % of 2-(methylamino)ethanol and dimethylethanolamine, representing a calibration curve for ion chromatography analysis.**

nolamine (20% by wt); (2) ethanolamine (20%), methanol (60%), water (20%); (3) ethanolamine (100%); and (4) water (100%), and are listed in Table 1.

The water/methanol/ethanolamine (99.5%) showed a slightly higher removal efficiency as compared to water/ethanolamine (99.1%) due to the greater solubility of methyl bromide in methanol. Methyl bromide is freely soluble in alcohol, whereas its solubility in water is only 1.75 g/100 g of solution.[10] Ethanolamine (100%) resulted in the highest removal efficiency (99.9%) utilizing 9.6 equiv as compared to 3.2 equiv for scrubber solutions (1) and (2). In the case of pure water as a scrubber it was shown that essentially all of the methyl bromide passed through the scrubber. The aqueous ethanolamine (20%) scrubbing medium is preferred and recommended for pilot-plant usage since the reaction byproducts (2-(methylamino)ethanol, dimethylethanolamine, and hydrogen bromide salts) are soluble in water and the solution is more suitable for wastewater treatment disposal (than methanol-containing waste streams). Thus 20% ethanolamine provides a good balance between high removal efficiency, ease of waste treatment, and lower VOC loss. In Figure 5, a typical methyl bromide profile is obtained for inlet flow and outlet flow during a laboratory experiment. On the basis of the measured flows the efficiency of the 20% aqueous ethanolamine was 99.1%. In summary, ethanolamine solutions were shown to be highly effective for removal of methyl bromide vapors, with measured control efficiencies of >99%. In addition, the gas−liquid contact time in the laboratory is considered shorter than in the pilot plant, and thus it was expected that pilot-plant efficiencies would exceed our laboratory efficiencies.

3.2.c. Ion Chromatography Analysis. In addition to analyzing the aqueous ethanolamine scrubber inlet and outlet using MS, ion chromatography (IC) was utilized to verify that methyl bromide was being consumed. Standards were prepared gravimetrically by bubbling varying amounts of methyl bromide (wt %) into the aqueous ethanolamine (20%) scrubber solution. IC analysis identified two byproducts from the aqueous ethanolamine (20%) scrubbing of methyl bromide: 2-(methylamino)ethanol, and dimethylethanolamine (Table 2). IC results have shown methyl bromide molar recoveries of >95% in the laboratory, on the basis of analysis of the two byproducts above. Table 2 represents the IC standards that were made and plotted in Figure 6. In a separate experiment, the scrubber solution was weighed before and after the introduction of methyl bromide, and this value was consistent with the calculated amount of methyl bromide delivered by the flow control meter. This experiment verified the flow meters were accurate and that methyl bromide was being consumed by the scrubber solution.

3.2.d. Silver Nitrate Titrations to Determine Bromide Content. An alternative method of calculating recovered mass from the methyl bromide/aqueous ethanolamine scrubbing

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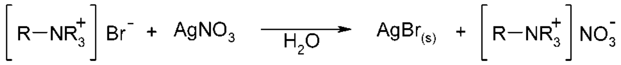
(10) Braker, W.; Mossman, A. L. *Matheson Gas Data Book*, 6th ed.; Matheson Gas Products: East Rutherford, NJ, 1980; p 456.

Table 2. **Ion chromatography results: methyl bromide scrubber standards prepared gravimetrically by bubbling MeBr into 20% ethanolamine solution**

MeBr input		scrubber solution		2-(methylamino) ethanol		dimethyl ethanolamine			
MeBr %[a]	mol	initial weight[b] (g)	final weight (g)	wt (%)[c]	mol MeBr consumed[d]	wt (%)[c]	mol MeBr consumed[e]	total mol MeBr consumed	MeBr recovery (%)[f]
0.185	0.0021	107.9	108.10	0.165	0.0024	0	0	0.0024	**112.7**
0.537	0.0061	107.36	107.94	0.39	0.0056	0.016	0.00039	0.0060	**98.1**
0.674	0.0076	106.18	106.90	0.44	0.0063	0.029	0.00070	0.0070	**91.8**
1.400	0.0162	108.45	109.99	0.89	0.0130	0.1	0.00247	0.0155	**95.6**
1.897	0.0216	106.02	108.07	1.15	0.0165	0.18	0.00437	0.0209	**96.9**
2.509	0.0284	104.9	107.60	1.47	0.0211	0.25	0.00604	0.0271	**95.3**

[a] MeBr % = (MeBr input (g)/scrubber solution final weight (g)) × 100%. [b] Weighed from aqueous ethanolamine (20 wt %) stock solution. [c] Ion chromatography results, wt % of scrubber solution. [d] 2-(Methylamino)ethanol (MW = 75.1): *mol MeBr consumed* = **1** × mol 2-(methylamino)ethanol. [e] Dimethylethanolamine (MW = 89.1): *mol MeBr consumed* = **2** × mol dimethylethanolamine. [f] **% Recovery** = (total mol MeBr consumed/mol MeBr input) × 100%.

Scheme 3. **Reaction mechanism of ammonium bromide salts with silver nitrate, forming silver bromide as a precipitate**



$$\left[R-NR_3^+\right]Br^- + AgNO_3 \xrightarrow[H_2O]{} AgBr_{(s)} + \left[R-NR_3^+\right]NO_3^-$$

Table 3. **Pilot-plant scrubber conditions and results**

		scrubber additions					
		ethanolamine					
batch	SM input[a] (kg)	gal	equiv[b]	water (gal)	mass (kg)	% ethanolamine (wt %)	MeBr removal efficiency (%)
1	23.9	32	39	100	499	24.6	**99.9**
2	26.5	32	35	100	499	24.6	**99.9**
3	25.1	27	31	100	480	21.5	**99.8**
4	28.7	27	27	100	480	21.5	**99.9**
						av	**99.9**

[a] Compound A (MW = 463.75). [b] Ethanolamine (MW = 61.08, density = 1.012 kg/L) equivalents, based on SM.

solution is to quantify the amount of bromide in solution, as opposed to calculating the byproduct amines **2** and **3** (Scheme 2). One way to do this is by the addition of aqueous silver nitrate (Scheme 3), which reacts with the ammonium bromide salts and precipitates silver bromide, leaving the resulting ammonium nitrates in solution.

Immediately upon addition of an aqueous solution containing 4.80 g (1.2 equiv based on methyl bromide) of silver nitrate (MW = 169.88) to the aqueous ethanolamine (20%) scrubber solution, silver bromide (MW = 187.78) precipitated as a white solid. It should be noted that silver bromide is a light-sensitive solid, such that all manipulations were done with the lights off whenever possible. The solid was collected on a Buchner funnel and dried in a vacuum oven at 40 °C with a slow nitrogen sweep. Following filtration and drying, 3.90 g of silver bromide was recovered, corresponding to approximately 95% yield based on methyl bromide input.

3.3. Scale-Up Results (Pilot Plant). *3.3.a. On-Line Monitoring of Methyl Bromide Using MS.* The scrubber solution makeup and starting material inputs for each batch used in the pilot plant are shown in Table 3, whereby the ethanolamine equivalents (relative to methyl bromide) ranged from 27 to 39 and the wt % aqueous ethanolamine used was 21.5−24.6%. Figure 7a shows the MS raw data response for methyl bromide and nitrogen during batch 4, whereby the methyl bromide response on the outlet of the scrubber is 3 orders of magnitude lower than the inlet response. Methyl bromide scrubber removal efficiencies for each data point were calculated by comparing the inlet response ratio (*m*/*z* 94/28) to the outlet response ratio, resulting in >99.5% removal. Figure 7b shows the methyl bromide offgas profile for batch 4 (obtained from Figure 7a and using eq 6a), which starts during reactor heat-up to 95 °C ($t = 1$ h), then increases to peak flow rate ($t = 6$ h), followed by an exponential decrease with an estimated decay constant of 0.08/h. The decay constant (0.08/h) was calculated as the slope of the natural log of methyl bromide flow rate versus time (h) line during exponential decrease ($t = 6-24$ h). The decay constant was applied to estimate the methyl bromide scrubber efficiency for batches 1−3 as well. The methyl bromide gas flow was estimated assuming 1 mol of the methyl halide (CH_3) is released per mol of substrate (compound A) during batch 4. The methyl bromide flow rate does not reach baseline ($t = 25$ h, reaction completion) due to the lack of a nitrogen "sweep" (e.g., scrubber draft pressure) and large headspace present during the reaction. Note: the headspace volume in the 500-gal R-1 reactor was 450 gal. The scrubber draft pressure applied to R-1 was 8−20 in. H_2O. As shown, the scrubber draft pressure and temperature remained constant during the reaction period, resulting in a smooth methyl bromide response profile. The difference between the pilot-plant run (Figure 7b) and the laboratory run (Figure 4) is primarily the headspace-to-reaction volume ratio: laboratory = 1:1, versus pilot plant = 10:1. In addition we use a slight argon sweep in the lab where the pilot plant provided no sweep. The scrubber analysis resulted in >99.8% removal efficiency based on measured inlet and outlet methyl bromide concentrations for all 4 batches (Table 3).

3.3.b. Material Balance Analysis Using MS. By observing the demethylation reaction for the pilot-plant campaign (Scheme 1), there is 1 mol equiv of methyl halide (CH_3) and 1 mol equiv of hydrogen chloride (HCl) per mol of substrate (compound A) available to form reaction byproducts. Reaction offgas byproducts monitored during the pilot-plant reaction included methyl bromide (CH_3Br, *m*/*z* 94), methyl chloride (CH_3Cl, *m*/*z* 50), and hydrogen chloride (HCl, *m*/*z* 36). Figure 8 shows the offgas flow rate profiles

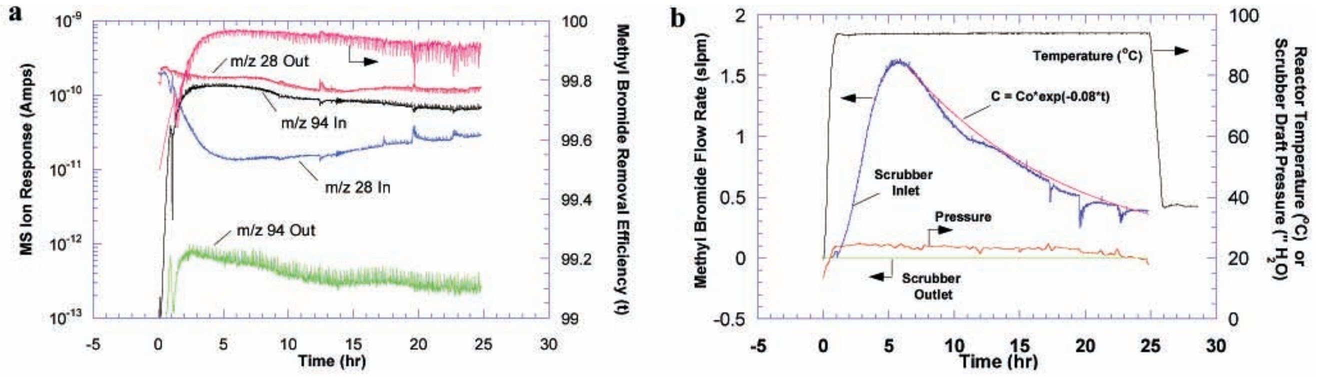


Figure 7. **(a) MS raw data response for methyl bromide (*m/z* 94) and nitrogen (*m/z* 28) in and out of the scrubber (left axis) during batch 4. The right-hand axis shows the methyl bromide removal efficiency by comparing the inlet response ratio to the outlet response ratio for each data point (*t*), whereby removal efficiency = (((94/28)In − (94/28)Out)/(94/28)In) × 100%. (b) Methyl bromide flow rate (L/min), temperature profile, and scrubber draft pressure profile during the demethylation reaction for batch 4. The methyl bromide flow rate reaches peak (1.6 L/min) at *t* = 6 h, then follows an exponential decrease with a decay constant of 0.08/h. Scrubber efficiency was calculated by comparing the area under the methyl bromide flow rate curve in and out of the scrubber. Scrubbing efficiency = ((1194 L − 0.68 L)/1194 L) × 100% = 99.9%.**

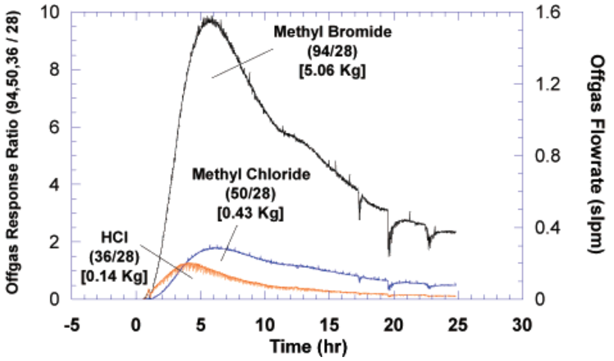


Figure 8. **Scrubber inlet offgas response ratio and offgas flow rate profile for methyl bromide, methyl chloride, and HCl. The flow rate profiles were calculated assuming one mol of methyl (CH_3) is released per mol of substrate (compound A). The total mass for each offgas (shown in brackets) is calculated as the area under the inlet flow rate curve.**

for all three gases, whereby methyl chloride and HCl flow rates are much smaller compared to the methyl bromide flow rate profile. The offgas response ratio represents a relative concentration. The total value of gas flow for each byproduct was estimated by assuming that 1 mol of the methyl halide (CH_3) is released per mol of substrate (compound A) during batch 4 (Note: reaction completion was verified during pilot-plant runs). Scrubber removal efficiencies for methyl chloride and HCl were calculated as 99.9 and 92.2%, respectively, using the same methodology as methyl bromide removal efficiency calculations.

The resulting material balance for methyl halide (CH_3) and chloride (Cl) is shown in Table 4. On the basis of a batch 4 compound A input of 28.7 kg (0.062 kmol), there are 0.062 kmol of methyl halide and 0.062 kmol of chloride available. The amount of the methyl halide which forms methyl bromide is 0.86 equiv, compared to 0.14 equiv for methyl chloride. The amount of chloride released as offgas is 0.20 equiv (0.14 equiv as methyl chloride, 0.06 equiv as HCl), with an estimated 0.80 equiv remaining in solution. In summary, these data obtained from pilot-plant runs are consistent with the demethylation laboratory results discussed above and shown in Figure 4.

Table 4. **Methyl halide (CH_3) and chloride (Cl) material balance: batch 4**

constituent	methyl halide (equiv)	chloride (equiv)
methyl bromde offgas	0.86[a]	–
methyl chloride offgas	0.14[a]	0.14[a]
HCl offgas	–	0.06[a]
HCl in solution	–	0.80[b]
totals	**1.0**	**1.0**

[a] Amount based on area under inlet flow profile curve, assuming 1 equiv of compound A is available for methyl halide generation. [b] Material balance closure based on 1 mol of HCl per mol of substrate (compound A).

3.3.c. Ion Chromatography Analysis (Pilot Plant). In addition to MS, an independent method (ion chromatography) was developed to verify the amount of methyl bromide that was being consumed by the aqueous ethanolamine scrubber solution during the pilot-plant reactions. Ion chromatography analysis has verified that methyl bromide (in addition to methyl chloride vapors) was consumed, whereby the overall methyl halide recovery over all 4 batches was 94%. The theoretical methyl halide recovery is 100%, since the demethylation reaction was shown to go to completion (i.e., compound A remaining = 0%). The overall methyl halide recovery was estimated by comparing the total moles of methyl halide available (based on compound A input) to the amount of methyl halide consumed by the scrubber based on the 2-(methylamino)ethanol and dimethylethanolamine IC measurements. Methyl halide recovery results for IC analysis for batches 1 through 4 are shown in last column of Table 5 and ranged from 62 to 127%.

At this point a discussion of the MS results (Table 3) versus the IC results (Table 5) is warranted. As discussed above, the MS provides relative concentrations on the inlet and outlet sides of the scrubber, which in the pilot plant indicated concentrations up to 3 orders of magnitude higher for methyl bromide on the inlet side than on the outlet side. One reason we believe that methyl bromide vapor as measured by *m/z* 94 does not rapidly return to baseline at the end of the reaction, as seen in Figure 7a, is because there

Table 5. **Ion chromatography results: pilot plant**

		mono[a]		di[b]					
batch	scrubber weight (kg)	wt %[c]	kmol Me consumed	wt %[c]	kmol Me consumed	total kmol Me consumed	SM Input[d] (kg)	kmol Me available[e]	methyl recovery (%)[f]
1	499	0.565	0.0378	0.01	0.00113	0.0389	23.9	0.0515	75
2	499	0.84	0.0563	0.0355	0.00401	0.0603	26.5	0.0571	106
3	480	0.49	0.0315	0.019	0.00206	0.0335	25.1	0.0541	62
4	480	1.1	0.0711	0.0685	0.00746	0.0786	28.7	0.0619	127
					totals	**0.211**		**0.225**	**94%**

[a] 2-(Methylamino)ethanol (MW = 75.1): *kmol methyl (Me) consumed* = **1** × kmol 2-(methylamino)ethanol. [b] Dimethylethanolamine (MW = 89.1): *kmol methyl (Me) consumed* = **2** × kmol dimethylethanolamine. [c] Ion chromatography results, wt % of scrubber solution. [d] Compound A input (MW = 463.75). [e] kmol Me available = SM input (kg) × [Me (MW = 15)/SM (MW = 463.75)]. [f] **% methyl recovery** = (total kmol methyl consumed/kmol methyl available) × 100%.

is residual vapor present in the headspace and vent-lines. The vapors are not swept with nitrogen flow but rather only a slight vacuum (20 in. H_2O) is created downstream of the scrubber to pull any excess vapor. This would explain why batch 1 resulted in only 75% of the theoretical amount of methyl bromide coming in contact with the scrubber solution. Approximately 25% remained in the reactor headspace and vent lines (remaining amount of methyl bromide gas was consistent, using ideal gas law calculation). In the present campaign we had a significant amount of headspace relative to reaction volume—only 50 gal of reaction mixture in a 500-gal tank. In addition, the entire system upstream of the scrubber is sealed between batches. The scrubber solution is also replaced with fresh ethanolamine solution between batches. Thus, when batch 2 began, we believe the residual vapors that remained at the end of batch 1 were forced into the scrubber solution. The final analysis of batch 2 appears to be consistent with this theory, provided some residual vapor was left behind at the end of batch 2. Between the batches there may be varying amounts of residual vapors left behind, depending on draft pressures employed during the runs. At the end of the campaign (batch 4) nitrogen was used to purge the reactor, filter, and all vent lines through the scrubber. Thus, residual vapors left over from batches 3 and 4 would have been forced into the scrubber (Note: concentration of methyl bromide (m/z 94) was 2 orders of magnitude higher between batches than at the start of the campaign, indicating residual methyl bromide). This explains the 127% theoretical recovery for batch 4. In addition, the magnitude of the MS scrubber inlet concentration response (area under m/z 94/m/z 28 profile) correlated with IC results for batches 1 through 4. In summary, an excellent methyl halide recovery balance is achieved for the direct analysis of the scrubber byproducts of methyl bromide with ethanolamine versus starting material input over all 4 scrubber batches as is appropriate due to the process procedures used during the campaign.

The IC results and vapor phase MS results obtained from the pilot plant highlights an important point. In the lab testing, where we have a controlled flow rate of reference gas (argon) that is blended with the methyl bromide, there is an established flow rate of gases in and out of the scrubber. On the other hand if the flow of gas stops, the MS continues to detect levels of gases on the inlet and outlet side in proportion to their concentration. These measurements do not ensure that flow is necessarily occurring through the scrubber. More important, the MS provided real-time measurements that showed that methyl bromide concentrations at the outlet of the scrubber were negligible. In short, a reference gas such as nitrogen or argon with a constant flow rate will ensure that gases are swept through the scrubber and that the MS method can be used to calculate an actual flow rate in and out of the scrubber.

3.3.d. Demethylation Reaction Completion Analysis (Pilot Plant). The reaction completion time during laboratory studies was shown to be 12−15 h. By observing Figure 7b (batch 4 reaction) the majority of the methyl bromide has evolved after 12−15 h, and the slow decrease towards baseline is primarily due to the lack of a sweep present and the large headspace effect during the reaction. On-line mass spectrometry could potentially be used as an indicator for reaction endpoint, which could significantly reduce the batch time (Note: reaction time during the campaign was set at 24 h). A nitrogen sweep would help move the methyl bromide through the reactor headspace into the scrubber more rapidly, and MS end point detection could be enhanced.

3.3.e. Recommendations for MS Monitoring On-Scale. (1) Reduce reactor headspace during reaction, this will increase the correlation between reaction endpoint and methyl bromide concentration detected by MS. (2) Provide a small nitrogen sweep preferably with a known flow rate through the scrubber system. (3) Maintain steady scrubber draft inlet pressure during on-line monitoring for stabilization of the MS signal. (4) Purge after the reaction to displace all residual methyl bromide vapors to the scrubber before proceeding to the next batch. (5) Utilize MS as a quality-control tool to ensure methyl bromide vapor has been purged from system before the vessel is opened.

4. Conclusions

Methyl Bromide is a VOC produced during demethylation reactions, that poses adverse safety and environmental issues. Development of the methyl bromide scrubber system using ethanolamine resulted in a successful transfer of the MS technology from the laboratory to the pilot plant. The MS on-line monitoring showed >99% removal of methyl bromide at both scales. The ability to monitor the offgas profile on-line for both the inlet and outlet of the scrubber has been demonstrated, thereby ensuring a safe and environmentally benign process during production. In addition, the ability to monitor multiple offgases (including methyl bromide, methyl chloride, and HCl) and determine a material balance estimate by MS was also shown. Ion chromatography (IC) and silver nitrate were used to confirm scrubber composition and verified that methyl bromide and methyl chloride were being trapped. The aqueous ethanolamine (20%) scrubber medium effectively converted the methyl bromide offgas to the 2-(methylamino)ethanol and dimethylethanolamine byproducts (and associated HBr salts) for aqueous waste disposal. Another application for MS monitoring during demethylation reactions is to utilize the methyl bromide offgas profile as an indicator for reaction completion, whereby significant time- and cost savings may be realized.

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