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Quantitation of alkyltrimethylammonium bromides in Bayer process liquors by gas chromatography and gas chromatography–mass spectrometry

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Abstract

A sensitive and specific capillary gas chromatographic (GC) assay has been developed for the quantitation of the series of quaternary ammonium (QA) compounds, dodecyltrimethylammonium bromide (C12QA), tetradecyltrimethylammonium bromide (C14QA) and hexadecyltrimethylammonium bromide (C16QA) in high ionic strength, highly alkaline solutions. The procedure employed a single dichloromethane extraction of the iodide ion-pairs of the QA compounds from pH-adjusted Bayer liquor, followed by injection (in methanol) onto the gas chromatography–mass spectrometry (GC–MS) system. Detection was based upon thermal dequarternisation of the QA–iodide complex in the injection port, with the corresponding tertiary amine (TA) analogue resolved by the GC system. Optimal extraction and GC conditions, as well as limits of detection and preliminary recoveries of these compounds, are reported. GC–MS, combined with injection of the pure TA analogues, was used to confirm the identities of the compounds eluted from the column.

Keywords: Bayer process liquor; Alkyltrimethylammonium bromide; Surfactants

1. Introduction

The Bayer process is used to refine bauxite to smelting grade alumina. Quaternary ammonium (QA) compounds have the potential to be used as surface active agents in this process. In particular, they seem well suited to the role of a sodium oxalate stabiliser [1,2]. At present, however, there is a lack of fundamental understanding regarding the chemistry of these types of compounds under Bayer conditions. There is also a lack of a sensitive and specific assay for the detection of QA compounds in Bayer liquor. Such an assay would allow the measurement of adsorption isotherms of QA compounds under Bayer conditions, furthering understanding of their Bayer chemistry.

QA compounds are of interest to researchers for many reasons. Their cationic nature combined with their dual hydrophilic/hydrophobic properties makes them ideally suited for use as surface modifiers and surface active agents, and has resulted in them being used in areas as diverse as hair and fabric conditioning [3,4] and weed control [5,6], while it is the cationic charged centre of QA compounds [7] that makes them significant in many biological systems. The potential of this family of compounds in in-

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dustrial processes is also quickly being realised [8–10].

The analysis and extraction of QA compounds, in particular those of biological significance, has received some attention since the late 1960s. Initial work focused upon the analysis of pure QA compounds using electron impact (EI) GC–MS, with identification via the thermal tertiary degradation product [11,12]. The first ion-pair extraction from a biological system was reported a little later [13], with a number of similar methods reported thereafter [14–19]. The low volatility of QA compounds has also seen research undertaken with the aim of obtaining mass spectra of the QA compounds themselves, i.e., not their thermal degradation products [20–26]. Ultraviolet–visible spectroscopy [27], liquid chromatography [6] and high-performance liquid chromatography [28,29] have also been used for the direct analysis of QA compounds. No work under Bayer (or Bayer-like) conditions has been reported.

The development and validation of an extraction and analysis method suited to QA compounds in Bayer liquor is thus reported. This method involves iodide ion-pair extraction of the QA followed by capillary GC–MS analysis. The extraction and analysis is relatively straightforward (considering the complexity of the background matrix), has a more than adequate limit of detection with good recoveries and seems well suited for use in the adsorption isotherm measurement of QA compounds in Bayer liquors.

2. Experimental

2.1. Chemicals

The analytical reagents dichloromethane (99.5%), methanol (99.8%, Rowe Scientific, Wangara, WA, Australia), eicosane (≈99%, Sigma-Aldrich, Castle Hill, NSW, Australia), hydrochloric acid (36%, Rhone-Poulenc, Clayton South, Vic., Australia), mannitol (99%, BDH, Kilsyth, Vic., Australia), glycine (98%, Aldrich, Milwaukee, WI, USA), anhydrous sodium sulfate (99.5%), sodium hydroxide (98.2%) and potassium iodide (99.5%, Sigma, Willetton, WA, Australia) were obtained commercially. The quaternary amines dodecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide and hexadecyltrimethylammonium bromide (≈99%, Sigma-Aldrich) and the tertiary amines dodecyldimethylamine (>95%), tetradecyldimethylamine (>90%) and hexadecyldimethylamine (>85%) (TCI Tokyo Kasei, Tokyo, Japan) were also obtained commercially.

2.2. Instruments

A HP5890 Series II Plus gas chromatograph (Hewlett-Packard, Palo Alto, CA, USA) equipped with an HP7673 automatic injection system (Hewlett-Packard) and coupled to a HP5972A mass sensitive detector (Hewlett-Packard) was employed, with the system operated in full scan acquisition mode at an ionization energy of 70 eV. A HP5ms cross-linked 5% phenylmethyl silicone fused-silica capillary column (25 m×0.25 mm I.D. and 0.25 μm film thickness; Hewlett-Packard) was used for component separation. Helium was used as the carrier gas at a linear velocity of 34 cm/s. Injector and detector temperatures were 300 and 280°C, respectively, using an injection volume of 2 μl (splitless mode). Injections were made into a standard splitless glass injection liner tube (4 mm I.D.) containing silanized glass wool. The oven temperature was held at 95°C for 2 min prior to being increased to 300°C at 8°C/min.

2.3. Bayer liquor

Investigation of Bayer liquor presents the analytical chemist with many challenges. Bayer liquors are extremely alkaline (pH>14), of high ionic strength (≈7 *M* [Na^+]), and contain a wide variety of organic compounds, including monobasic and dibasic acids, polyhydroxy acids, alcohols, phenols and carbohydrates. These organic compounds give Bayer liquor its characteristic deep brown–red colour and distinctive odour and, quite often, complicate analysis.

In this study, a stock Bayer liquor (Alcoa Kwinana refinery Kelly filtrate liquor) was used throughout. Standard liquor solutions were prepared by dosing this stock liquor with the required amount of each QA. Extractions were then performed on these

Table 1
Typical analysis of stock Bayer liquor (Kwinana Kelly filtrate)

Component	Concentration (mol/l)
NaOH	4.34
Na_2CO_3	0.52
Al_2O_3	1.03
NaF	0.05
NaCl	0.43
Na_2SO_4	0.25
TOC[a]	20[b]

[a] Total organic carbon.
[b] Expressed as g/l.

standard liquors. A typical analysis of the stock liquor can be seen in Table 1.

2.4. Procedure

To 5 ml of Bayer liquor containing standard QA compounds, 10 ml of deionised water and 2.5 g of mannitol were added. After mechanical shaking (5 min), the pH of the solution was adjusted to 10–12 by the addition of 2.25 ml of 5 *M* hydrochloric acid. Additional mechanical shaking (10 min) was then required to redissolve the precipitated aluminium hydroxide, prior to addition of 4.5 g of solid potassium iodide. Further shaking (10 min) was followed by a single addition of dichloromethane (12 ml; containing eicosane as the internal standard). The QA–iodide ion-pairs were subsequently extracted into the dichloromethane with further shaking (10 min). The aqueous layer was then discarded and the organic layer was dried over sodium sulfate and filtered. The extract was finally evaporated to dryness (40°C, <10 mbar) and taken up in 500 μl of methanol prior to chromatographic analysis. The procedure of Chan et al. [14] was used as reported, unless otherwise indicated.

3. Results and discussion

3.1. Quaternary ammonium bromide salts

In order to gain some insight into the chromatography of the alkyltrimethylammonium bromide salts, the three QA compounds were simply injected onto the GC–MS system in the form of methanolic solutions. The resulting chromatography was unsatisfactory to say the least. Not only did the QA compounds exhibit extremely poor responses (if any at all), the peaks in evidence showed a considerable degree of tailing. Attempts were made to overcome this problem through the use of different solvents. Both pyridine and dichloromethane were tested, with little or no improvement being evident.

This low response and peak tailing was suggestive of one of two things. The first possibility was that there was unusually high system activity towards these types of compounds. This was considered to be unlikely, however, QA compounds had not previously been analysed on the system in question, so no suitable reference was available. The second, and more likely, possibility was that the QA compounds were being injected as the bromide salts and not as the iodide salt ion-pair. Chan et al. [14] reported that both the bromide and the extracted iodide salts of neostigmine and pyridostigmine were being thermally dequarternised to their corresponding tertiary amine (TA) analogues upon injection in methanol. Isa and Yamada [23] also drew similar conclusions under somewhat different conditions. Other workers, however, only reported success with injection of the iodide ion-pair [17,19]. In this case, it was concluded that the bromide anion was not a sufficiently strong nucleophile (under system conditions) to yield a tertiary analogue and an alkyl halide from the quaternary salt. GC analysis of the pure bromide salts was thus considered impossible.

3.2. Extraction from a simple system — water

Having had little success injecting the pure bromide salts, an extraction from water using the method of Chan et al. [14] was attempted. The ether wash employed by Chan and co-workers [14] to remove basic drugs and lipid-soluble material was deemed superfluous (due to the nature of the matrix). Other than that, their method was used, essentially unchanged. The pure QA compounds were dissolved in water over a range of concentrations and extracted as the iodide ion-pair. The resulting chromatography was considerably better than that achieved previously, with responses increasing by two orders of magnitude. Some peak tailing was still evident (see

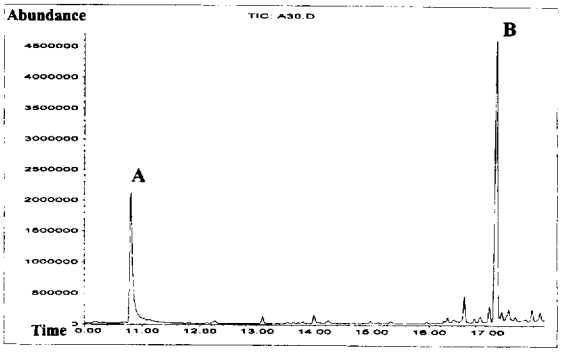

Fig. 1. Representative capillary gas chromatogram of a water extract showing (A) thermally dequarternised alkyltrimethylammonium bromide (C12QA; injected as an iodide ion-pair) exhibiting characteristic peak tailing and (B) phthalate impurity in dichloromethane. GC conditions are described in Section 2.

Fig. 1), however, this tailing did not limit the analysis. An attempt was made to reduce this activity by replacing the injection port liner, but this had little effect. Most importantly, linear responses were obtained for all three QA compounds tested over the range 0–10 ppm (in solution). Excellent correlations were obtained for C12QA, C14QA and C16QA, the values being 0.998, 0.999 and 0.998, respectively. Peak areas were obtained from extracted ion (m/z 58) chromatograms, the m/z 58 ion being characteristic of the QA dequarternisation product (see Fig. 2).

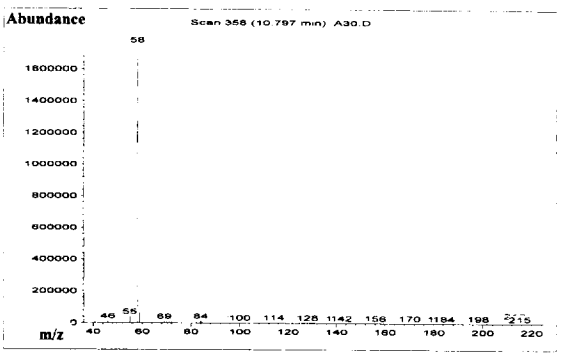

Fig. 2. Characteristic mass spectrum of thermally dequarternised, water extracted, alkyltrimethylammonium bromide (C12QA; injected as an iodide ion-pair complex), showing the m/z 58 ion used for QA quantitation.

3.3. Extraction from a complex system — Bayer liquor

Chan et al. [14] quoted an optimum extraction pH of 10–12. Given the high pH of Bayer liquor, it was obvious that some degree of pH adjustment was necessary. The very nature of Bayer liquors, however, makes any sort of pH adjustment difficult. Reducing the pH of a Bayer liquor has the unfortunate side effect of causing aluminium hydroxide ($Al(OH)_3$) precipitation. This is an undesirable situation in that such precipitation could result in the loss of QA analyte. An aluminium complexing agent was thus required. A number of options were available. Citric, gluconic and tartaric acids are known aluminium complexing agents, as are the sugars sucrose, glucose and mannitol [30]. Mannitol, in contrast to the others mentioned, is known to complex the aluminate ion ($Al(OH)_4^-$), as opposed to aluminium hydroxide itself, and thus does not release hydroxide upon complexation [30]. Mannitol was thus chosen for use as a complexing agent. (It was at this stage that the use of the KI–glycine buffer of Chan et al. [14] was questioned. Calculations showed that the glycine was present at such low concentration that it was considered unnecessary in the Bayer system. Potassium iodide, as the source of iodide, was subsequently added in solid form).

Thus, using mannitol to prevent aluminium hydroxide precipitation, hydrochloric acid (5 *M*) to reduce the pH to 10–12 prior to extraction, and solid potassium iodide as the source of iodide, the modified extraction procedure was used on a spiked Bayer liquor. The QA compounds were spiked into the Bayer liquor over a smaller concentration range to that used previously (0.4–4 ppm) and eicosane was added to the dichloromethane as an internal standard (see Fig. 3). Linear regression analysis was again used to construct calibration curves of the standard–internal standard peak area ratios versus concentration in the liquor. Linear responses were once more obtained for C12QA, C14QA and C16QA (0.999, 0.998 and 0.999, respectively).

Two of the QA compounds analysed by Chan and co-workers [14], neostigmine bromide and pyridostigmine bromide, were also used at this point, as internal standards in the QA-containing matrix. However, the chromatography of these two com-

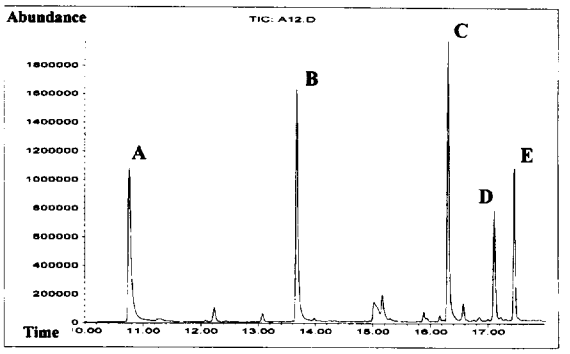

Fig. 3. Representative capillary gas chromatogram of Bayer liquor extract showing thermally dequarternised alkyltrimethylammonium bromides (A) C12QA, (B) C14QA, (C) C16QA (all 4ppm; injected as iodide ion-pair complexes); (D) phthalate impurity in dichloromethane and (E) eicosane internal standard. GC conditions are described in Section 2.

pounds under the system conditions was not satisfactory for their use as internal standards.

3.4. Injection temperature

It was at this stage that the effect of injection temperature on system chromatography was investigated. Extracted QA–iodide salts were injected at 250, 300 and 350°C, with no significant change in the chromatographic results being observed, supporting the hypothesis that 100% conversion of QA to TA had occurred in the injection port. An injection temperature of 300°C was used thereafter, as this temperature was routinely used for other, unrelated, GC–MS work. A temperature of 250°C, however, would have been quite adequate in this case.

3.5. Peak identification

Peak identification was accomplished using the TA analogues of the respective QA compounds. The TA analogues were simply injected onto the column in methanol and retention times were used to confirm peak identities (see Table 2). The mass spectra of the extracted QA compounds were also identical to the mass spectra of the respective TA analogues (see Fig. 4), confirming the aforementioned peak assignments and verifying the hypothesis of thermal de-

Table 2
Retention times of extracted QA compoundss and predicted TA analogues

Extracted QA	t_R (min)	TA Analogue	t_R (min)
C12QA	10.81	C12TA	10.77
C14QA	13.74	C14TA	13.69
C16QA	16.36	C16TA	16.33

quarternisation of the QA compounds to their respective TA analogues in the injection port.

3.6. Reproducibility, recovery and limit of detection

Replicate injections of the respective TA analogues were made to test the precision and reproducibility of the system. Both were found to be excellent and more than adequate for the QA analy-

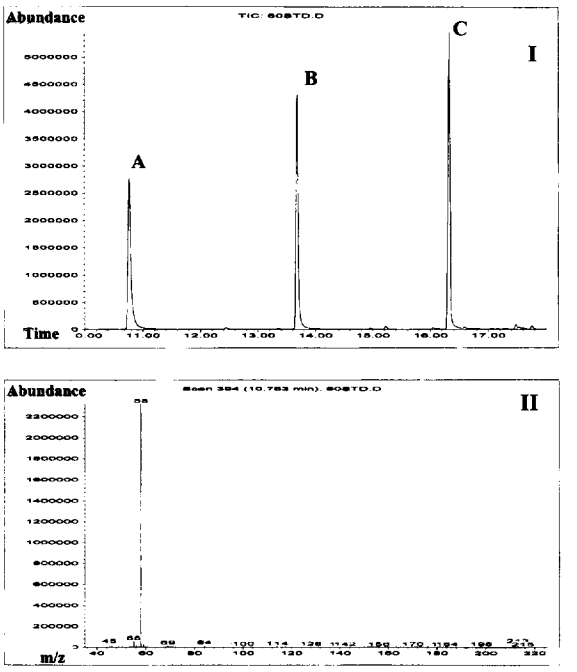

Fig. 4. Representative capillary gas chromatogram (I) of alkyldimethylamine standards injected in methanol (A) C12TA, (B) C14TA, (C) C16TA and the corresponding mass spectrum (II), showing the characteristic m/z 58 ion (C12TA). GC conditions are described in Section 2.

Table 3
Injection precision and reproducibility of TA analogues in methanol

Injected TA	R.S.D. (%)[a] (10 ppm)[b]	R.S.D. (%)[a] (60 ppm)[b]
C12TA	0.45	0.32
C14TA	0.19	0.26
C16TA	0.29	0.24

[a] Number of injections = 10.
[b] Concentration of injected TA.

sis (see Table 3). A similar test was performed to determine the reproducibility of the extraction itself. Replicate extractions were undertaken, the results showing them to be both precise and reproducible.

Preliminary calculations, based on the extractions from Bayer liquor described previously, gave extraction recoveries of the order of 75–85% for the three QA compounds examined (see Table 4). These calculations, based upon the assumption of 100% conversion of QA to TA in the injection port, show the extraction procedure to be quite efficient and are in agreement with the results of other authors [14,25]. It must be noted here, however, that extractions from liquors with QA concentrations above those reported, exhibited lower recoveries and that calibration curves tended towards non-linearity. This reduction in extraction efficiency at higher QA concentrations may be attributable to micelle formation, and the phenomenon is currently being investigated. Unfortunately, little research into the area of micelle formation of these types of compounds in such complex systems has been reported. In simple aqueous systems, the critical micelle concentration (CMC) of these types of compounds is typically in the order of 10^{-2}–10^{-4} M [31]. In Bayer liquors, however, preliminary results suggest that the CMC values are of two orders of magnitude less than the aforementioned values.

The limits of detection for the three QA compounds, based upon the tertiary dequarternisation products, were determined to be 14.4, 13.9 and 13.5 ng/ml of liquor for the C12QA, C14QA and C16QA compounds, respectively. Lower limits of detection were obtainable, but considered unnecessary in the context of the proposed adsorption isotherm analysis.

Table 4
Extraction recoveries of QA compounds in Bayer liquor

Extracted QA	Recovery (%)	R.S.D. (%)[a]
C12QA	84.2	9.1
C14QA	87.4	7.2
C16QA	73.3	6.7

[a] Number of extractions = 5.

4. Conclusion

A straightforward, accurate method for the quantitation of dodecyltrimethylammonium bromide (C12QA), tetradecyltrimethylammonium bromide (C14QA) and hexadecyltrimethylammonium bromide (C16QA) in Bayer liquor has been developed. This extraction and analysis method seems well suited to the measurement of the adsorption isotherms of these QA compounds on sodium oxalate under Bayer and Bayer-like conditions.

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