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Journal of Chromatography A, 1061 (2004) 93–98
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Methyl methacrylate in poly(methyl methacrylate)—validation of direct injection gas chromatography

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Received 15 July 2004; received in revised form 25 October 2004; accepted 25 October 2004

Abstract

Gas chromatography (GC) was investigated for the determination of residual methyl methacrylate (MMA) in heat-processed poly(methyl methacrylate) (PMMA) denture base material emphasizing recovery and validation. Standard solutions of MMA and emulsion-polymerized PMMA in dichloromethane were analysed, before and after distillation by a room-temperature air stream into a liquid nitrogen trap, and in the presence of PMMA by direct injection. Quantitative NMR analysis using dimethyl sulphoxide as internal calibration standard in deuterated chloroform solutions provided validation. Good concordance was observed between results under all conditions; no problems arose from direct injection of PMMA solution for GC. Good straight line responses in log–log plots were generally observed. For GC and MMA: log–log calibration curve (slope: 0.9552 ± 0.0051, r^2: 0.9992, $n = 32$) indicated some non-linearity ($t = 8.875$, $p \sim 4 \times 10^{-10}$). Distillation gave slope: 0.9751 ± 0.0213 (NS versus unity; $t = 1.172$, $p > 0.25$). For PMMA solutions, distillation (r^2: 0.9301) gave greater scatter than direct injection (r^2: 0.9704). For NMR: log–log plot of calculated versus actual MMA (slope: 0.9363 ± 0.0157, r^2: 0.9969, $n = 13$) again indicated non-linearity ($t = 4.0682$, $p = 0.0019$). PMMA solutions gave slope: 0.9477 ± 0.0328, $r^2 = 0.9858$ (NS versus unity; $t = 1.5941$, $p = 0.13$). Determination of MMA in PMMA by GC is recommended.

Keywords: Methyl methacrylate; Direct injection gas chromatography; Poly(methyl methacrylate); Quantitative NMR

1. Introduction

Since the early 1950s, dentistry has been using large quantities of poly(methyl methacrylate) in the form of denture bases. These are prepared by processing a mixture of methyl methacrylate (MMA) and polymer (∼1:3 by mass), with benzoyl peroxide as a free-radical source for initiation, at temperatures in the range 70–100 °C in a mould under slight pressure. A great deal of attention has been paid to the question of minimizing the residual MMA, which typically lies in the range ∼0.1–5% by mass, as this is a source of both mechanical effects, softening and weakening [1,2], and biological problems arising from the irritancy of MAA [3,4]. Accordingly, a suitable analytical technique is required for the routine determination of MMA in PMMA for such studies to proceed effectively.

Several approaches are possible and have been used: bromine titration, IR, high-pressure liquid chromatography (HPLC), and—most commonly—GC. Bromine titration [5–8] depends on the electrophilic addition of Br_2 to the vinyl group and thus is not specific to MMA (cross-linking agents will also react), and may also be prone to reaction with impurities. It is also a time-consuming titration. Infrared spectrophotometry [9] in principle is workable but given the non-adherence to Beer's law at higher concentrations and the overlapping absorption peaks in the complex spectra [10], and thus baseline difficulties, it appears not to have found favour in this context. HPLC [11,12] offers some advantages, such as avoidance of thermal degradation and sample recovery, although sample preparation is more onerous. For example, the mobile phase must be degassed. However, high-molecular weight polymer, especially those that have lower

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doi:10.1016/j.chroma.2004.10.088

solubility, such as the cross-linked acrylics relevant here, are more problematic. These would eventually block the column and must be separated from the solution. This is difficult other than by distillation, and this would increase the risk of losing monomer [13]. The cost of solvent required is also an issue. GC has been widely used [2,7,14–26] and appears to offer considerable convenience with good separations and short run times, but as it depends on an elevated column temperature thermal degradation needs to be considered, and only solutions of MMA extracted from PMMA have been analysed to date. GC depends on the calibration of what amounts to an arbitrary signal, that is the peak area from a non-absolute detector, but the sensitivity range can be very high.

While NMR is widely used for structure elucidation in organic chemistry, its use for quantitative analysis is not common although feasible. The direct proportionality of the signal to the number of atoms that produce it is a strong point, requiring only an appropriate internal standard of known concentration [10]; the analyte concentration is calculated using a standard equation [27,28]. In the present system, the vinyl protons of MMA are characteristic, with no expected interferences from similar groups in the matrix PMMA. Potentially, this is a rapid technique in that a calibration curve is unnecessary, but this may be offset by the set-up and scan times.

The analytical technique is not the only factor: the recovery and work-up of the sample to be analysed requires consideration. Thus, for GC, HPLC and NMR the sample commonly is in liquid form; IR is more flexible. The MMA from small fragments of PMMA has been extracted by refluxing with methanol [7] and this solution was injected into the GC. Alternatively, drilling to generate fragments with a large surface area for extraction has been used [15], but it was thought that the heat generated may have caused depolymerization so a hand drill at 70–80 rpm was preferred [17], despite a claim that no effect was found at up to 1700 rpm [15]. Such methods were criticized nevertheless because of the unavoidable heating [23]. Even so, the question of loss of monomer from large surface areas at elevated temperatures during preparation has received no comment; this would tend to offset increased MMA by loss from the surfaces where it is generated.

Depending on temperature, and given the essential equilibrium between PMMA and MMA [29], some monomer might be expected to appear as polymer in the solvent at the reflux temperature, while extraction from the fragments might generate it continuously. The selection of solvent has also been without explanation [7,14,30]. To get around these issues, samples have been cut into small pieces with a pair of nippers instead of drilling, and methanol, *N*,*N*-dimethylformamide (DMF), methyl ethyl ketone (MEK) and ethyl acetate compared at 60 °C [23]. Extracted MMA concentration was highest in MEK and lowest in methanol. MEK was also reported to extract more at lower temperatures, although this odd result was not explained. Solvent extraction efficiency is dependent in part upon the polarity of the solvent. The relative amount of monomer extracted by the solvents were: MEK > ethyl acetate > DMF > methanol, which sequence parallels the increasing polarity of the solvents; MMA is more soluble in nonpolar solvents. Lower extraction temperature was said to be preferred as the residual monomer may polymerize at higher temperature: the amount extracted decreased with increasing temperature. Zografakis et al. [31] believed that there was the possibility of degradation after injection into the GC of PMMA dissolved in the extract solution. After shaking homopolymer PMMA powder in methanol, samples were filtered 0, 1 and 4 times before injection. The unfiltered solution gave values about 1.6 times greater than the filtered. However, the injection (240 °C) and column (230 °C) temperatures were, in their view, high enough to cause depolymerization of the PMMA.

The conditions used for MMA extraction have varied widely (Table 1), although unfortunately much has not been documented. In some cases, a relatively large sample was used, although for routine analysis and, for example, attempts to understand spatial distribution of residual MMA in the denture (c. 15 g) as related to say, local thickness and temperature, small samples would be preferable. The question of which solvent to use remains open, although low temperature would seem more appropriate.

Accordingly, there were several objectives for the present work: to identify and verify a suitable recovery technique appropriate to the context, avoiding difficulties noted above, and to develop and validate a protocol for the analysis, avoiding evident problems.

2. Materials and methods

2.1. GC standard solutions

A representative denture base MMA product (Pro Base Hot, Ivoclar, Schaan, Liechtenstein) was used so that the analyses would be done under relevant background conditions. A stock solution of 2.0% (v/v) (18.9 mg/mL) of MMA was prepared in dichloromethane (analytical reagent grade, Riedel-de-Haën, Seelze, Germany) at 23 °C by pipetting 1.0 mL of MMA into a 50 mL volumetric flask (Grade A glassware), with dichloromethane added to the mark. Various standard solutions were prepared from this solution by serial dilution down to 0.0004% (v/v).

A range of standard solutions of PMMA (emulsion-polymerized powder, Struers, Kobenhavn, Denmark) were also prepared by dissolving 50–400 mg powder in 5 mL of dichloromethane (Riedel-de-Haën). Dichloromethane was chosen because of the high solubility and speed of dissolution of PMMA in it, comparison having first been made with a wide variety of solvents. It should be noted that, by virtue of the essential equilibrium with monomer exhibited by free-radical polymerizing systems [29], PMMA always contains a small amount of MMA. The PMMA powder used here was considered to be well-equilibrated and therefore have a fixed (but unknown) proportion of MMA.

Table 1
Summary of methods used for the extraction of residual monomer (MMA) from PMMA

Reference	Analytical technique	Method of extraction	Sample mass (g)	Solvent	Volume (mL)	Duration (h)
[5]	Br titration	[a]	[a]	[a]	[a]	[a]
[6]	Br titration	[a]	[a]	[a]	[a]	[a]
[7]	GC	Reflux	6.0	Methanol	10.0	4
[14]	GC	Reflux	5.0	Methanol	[a]	6
[15]	GC	Reflux	0.1–0.4	Methanol	10	1
[16]	GC	Reflux	[a]	[a]	[a]	[a]
[17]	GC	Reflux	0.1	Methanol	10	1.25
[18]	GC	Reflux	0.5	Methanol	10	3
[19]	GC	Reflux	[a]	Methanol	[a]	[a]
[22]	GC	Reflux	[a]	Methanol	[a]	[a]
[9]	IR	[a]	[a]	[a]	[a]	[a]
[23]	GC	4 °C	0.2	Methyl ethyl ketone	5	96
[24]	GC	[a]	2	Methanol	[a]	[a]
[25]	GC	Reflux	>0.4	Methanol	[a]	[a]
[2]	GC	Reflux	1.0	Methanol	20	6
[11]	HPLC	Room temperature	0.1	Tetrahydrofuran	10	48
[26]	HPLC	21 ± 2 °C	0.65	Acetone	10	72
[12]	HPLC	23 °C	0.65	Acetone	10	72 ± 2

[a] No information given.

2.2. Distillation

A primary concern was the accurate recovery of the MMA in a processed PMMA sample, with neither loss of MMA nor generation by decomposition interfering during the extraction process. In addition, there was the concern that decomposition of any PMMA in the hot GC would compromise the results. To address the first point, a cold distillation technique was devised. This entailed distilling a ∼1 mL portion of the test solution into a liquid-nitrogen U-tube cold trap in a slow stream of dry, room-temperature air, monitored by a downstream bubble "flow indicator", and then analysing the condensate.

Two kinds of trial were conducted. Firstly, gravimetric determination of the efficiency of transfer from distillation vessel to the trap was made, for starting solutions of MMA only ranging from 0.01 to 0.08% (v/v) at a variety of bubble rates, both with and without a water bath at 25 °C being applied to the distillation vessel. The time to dryness in the distillation vessel was noted. Secondly, standard solutions of PMMA were distilled to determine the recovery of the included 'equilibrium' MMA.

2.3. GC analysis

The GC system (HP 5890, Hewlett-Packard, Boise, ID, USA) had a capillary column (HP 19091F-115, Hewlett-Packard) with polyethylene glycol as the stationary phase, film thickness 0.52 μm, length 50 m (to obtain good resolution of solvent and analyte peaks) and internal diameter 0.32 mm. The flame-ionization detector output was taken to an integrator (HP 3395, Hewlett-Packard). Duplicate manual injections of 2.0 μL portions of the solution to be analysed were made by micro-syringe (2933087, Hamilton, Reno, NV, USA). The glass wool-packed, deactivated port liner (5183-4647, Agilent, Palo Alto, CA, USA) was changed weekly, roughly every 50 injections for this work. Operating settings were adjusted to obtain good working conditions for the analysis. After some exploration, and based on technical advice received, the following were used for all analyses: oven temperature, 75 °C; injection and detector temperatures, 120 °C; column head pressure, 100 kPa; carrier gas, helium; column flow rate 2 mL/min, split ratio about 40:1 for total flow rate 82.4 mL/min.

The following analyses were undertaken:

(1) Calibration of GC using standard solutions of MMA.
(2) Recovery trials for cold-distilled MMA standard solutions.
(3) Analysis for 'equilibrium' MMA in PMMA standard solutions after distillation.
(4) Analysis for 'equilibrium' MMA in PMMA standard solution using direct injection into the GC.

2.4. NMR standard solutions

Standard MMA (Pro Base Hot, Ivoclar) solutions were prepared in deuterated chloroform containing 0.03% (v/v) tetramethyl silane (TMS) as internal standard (Armar, Döttingen, Germany) at concentrations from 0.01 to 14% (v/v), with dimethyl sulfoxide (DMSO) of similar concentration included. A micro-pipette (3110000.064, Eppendorf, Hamburg, Germany) for the range 100–1000 μL, and a micro-syringe (85200, Alltech, IL, Australia) for volumes of 0.1–5 μL, were used.

PMMA (Struers) standard solutions were similarly prepared with 50–450 mg powder dissolved in 5 mL of deuterated chloroform (Armar), to which was added 0.2 μL DMSO.

2.5. NMR analysis

A 300 MHz NMR spectrometer (DPX 300, Brüker, Fallanden, Switzerland) was used with the following settings: number of scans, 8; dummy scans, 0; number of points, 2^{15}; sweep width, 5995.2 Hz; acquisition time, 2.7329 s; receiver gain, 16; and dwell time, 83.4 μs; at 300 K using 0.3 mL of solution.

The concentration of MMA was calculated using the following equation [27]:

$$\frac{C_{\mathrm{MMA}}}{C_{\mathrm{int}}} = \left(\frac{A_{\mathrm{MMA}}}{A_{\mathrm{int}}}\right)\left(\frac{N_{\mathrm{int}}}{N_{\mathrm{MMA}}}\right)\left(\frac{M_{\mathrm{MMA}}}{M_{\mathrm{int}}}\right) \quad (1)$$

where C is the concentration (mg/mL), A the value of the integrated signals for the protons of interest, N the number of protons per molecule giving the relevant signals, and M the molecular weight of the molecule concerned; the subscripts correspond to the analyte MMA or the internal standard ('int'). As there are two vinyl protons in MMA there are two separate signals ($\delta = 5.6$ and 6.1 ppm, w.r.t. TMS); the mean of the two was taken for A_{MMA}. The internal standard, DMSO, has $\delta = 2.6$ ppm w.r.t. TMS.

The following analyses were undertaken:

(1) Calibration check of NMR using standard solutions of MMA.
(2) Calibration check for 'equilibrium' MMA in PMMA standard solutions.

3. Results

For the GC calibration curve for the identified appropriate conditions, the slope of the fitted line in a log–log plot of peak area (arbitrary units) versus MMA concentration (mg/mL) was 0.9552 ± 0.0051 (r^2: 0.9992, $n = 32$). This slope is significantly different from unity ($t = 8.875$, $p \sim 4 \times 10^{-10}$), indicating appreciable non-linearity, but even so the narrow prediction interval suggests a reliable analysis using the logarithmic fitted curve.

The gravimetric distillation recovery results are illustrated in Fig. 1. It is evident that low bubble rates are necessary, but that the recovery was only of the order of 95% below a threshold of about 120 min^{-1}. The use of the water bath, to control the vessel temperature, had no evident effect. The distillation to dryness took between 15 and 110 min, depending on bubble rate.

The distillation analytical results for MMA standard solutions are shown in Fig. 2. It can be seen that, apart from two errant points at high bubble rates, concentration was preserved well (r^2: 0.9897). The slope (0.9751 ± 0.0213) does not differ significantly from unity ($t = 1.172$, $p > 0.25$). However, the trials using polymer solutions (Fig. 3) showed that whilst the distillation (r^2: 0.9301) and direct injection (r^2: 0.9704) results were generally consistent, the former gave greater scatter. The presence of the polymer did not appear to result in spurious values with direct injection. Neither slope differed significantly from unity (distillation: 0.9831 ± 0.0674, $t = 0.2508$, $p > 0.80$; direct injection: 1.0381 ± 0.0454, $t = -0.8397$, $p > 0.40$).

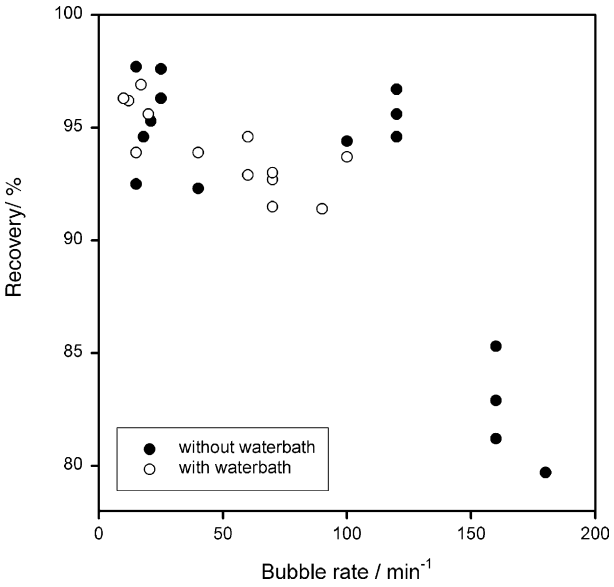

Fig. 1. Gravimetric recovery of MMA solution by distillation with respect to flow rate of room-temperature air stream.

The slope of the log–log plot of calculated versus actual MMA concentrations (mg/mL) for the NMR calibration check was 0.9363 ± 0.0157 (r^2: 0.9969, $n = 13$). This differs significantly from unity ($t = 4.0682$, $p = 0.0019$), indicating a non-linear response. The corresponding analysis of polymer solutions is shown in Fig. 4 (r^2: 0.9858), in which figure comparison is made with the direct injection GC results. The slope here (0.9477 ± 0.0328) does not differ significantly from unity ($t = 1.5941$, $p = 0.13$).

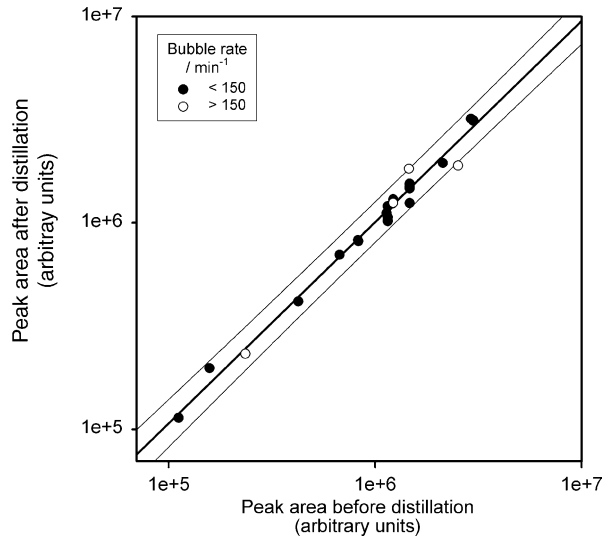

Fig. 2. Concordance of GC analysis before and after distillation of standard solutions of MMA. Fitted regression line shown for bubble rate <150 min^{-1}, with 99% prediction interval ($n = 24$) (solid symbols).

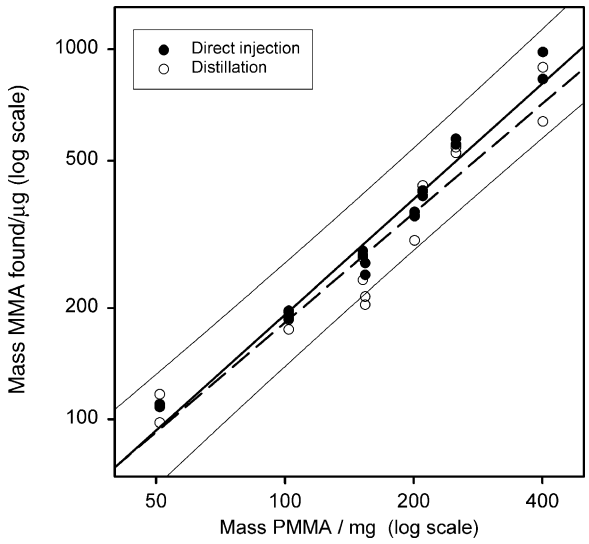

Fig. 3. Check GC analysis for 'equilibrium' MMA by direct injection and after distillation of standard solutions of PMMA. Regression lines (broken for distillation) shown for both ($n = 18$ for both), 99% prediction interval for direct injection only.

4. Discussion

It would appear from the MMA GC calibration that there are no particular problems in the basic analysis, once having chosen appropriate operating conditions. The recovery of MMA by distillation was disappointing in terms of the gravimetric results (Fig. 1) as it could not be assumed that fractionation had not occurred, resulting in biased concentrations in the condensate (bp CH_2Cl_2: 40 °C; MMA: 100.5 °C), although the analysis merely indicates somewhat greater scatter (Fig. 2). It is this extra scatter that probably accounts for the poorer results with the distilled PMMA standard solutions (Fig. 3).

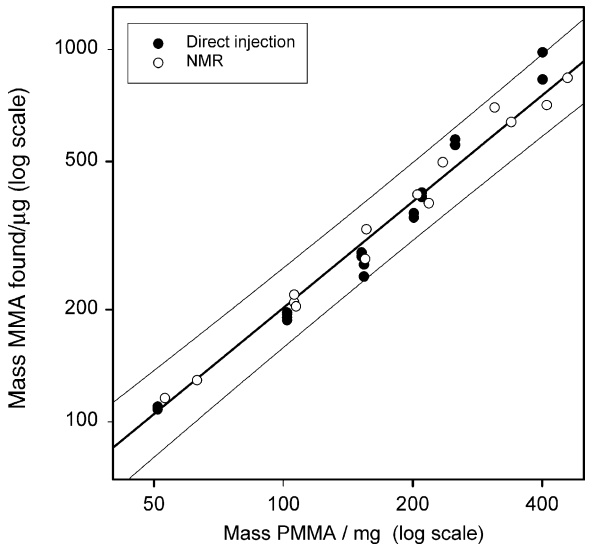

Fig. 4. Concordance of NMR and GC analyses for 'equilibrium' MMA of standard solutions of PMMA. Regression line and 99% prediction interval shown for NMR data only ($n = 14$) (GC data as in Fig. 3).

The distillation process was not technically difficult, but despite care being taken no improvement on the present results could be obtained. The extra handling involved, and the need to preserve the very volatile solvent quantitatively, necessarily compromise the results. Even so, as a matter of principle, such results are likely to be more accurate than extractions over long periods with hot solvents, both in terms of analyte preservation and avoidance of depolymerization, as well as not requiring the specimen to be in small fragments. The total dissolution technique used here ensured immediate complete 'extraction'. In addition, the distillation was time-consuming (although if the outcome were strong enough this could be offset with multiple units, but it also involved liquid nitrogen and its hazards). The outcome seems not to warrant this path being taken for routine purposes.

Given the possibility of the decomposition of PMMA to MMA, it was feared that the direct injection of a solution containing PMMA would result in gross over-reporting of concentrations. In the event, this was unfounded. It can be rationalized by noting that even at 120 °C, the injection port temperature, the depolymerization will be kinetically-limited, given that the equilibrium is still expected to be well in favour of polymer, the ceiling temperature being about 160 °C [29]. Thus, the decomposition which is expected to be occurring will be on a time-scale very long in comparison with that of the volatilization of the solvent and original MMA, and their entry into the column. Any further MMA will thus result in an elevated background rather than an elution peak and so be taken care of by the instrument's background (baseline) correction. It was concluded that direct injection of PMMA-containing solution was a viable technique.

The calibration curve for the NMR analysis indicated that this too is a viable technique, and although greater scatter was observed for the analyses of polymer solution, the results here are concordant with the direct injection of PMMA solution GC results, validating the idea that decomposition of PMMA is not a problem there.

NMR absorptions depend on relaxation time, radiofrequency source intensity, and scan rate. Protons in different environments have different relaxation times and slight deviations from exact integer ratios are commonly found in the signal intensities, and were in fact observed here. If the radiofrequency source is intense and the scanning rate low, signal saturation may occur and lead to low integral values. Further, at low MMA concentration, the weaker signal has to be greatly amplified and the spectrum has a noisy baseline, leading to inaccurate integral values as baseline noise is also integrated [32]. As a result, there was a discrepancy between the actual and calculated [MMA] for the more dilute solutions. Consequently, the effective detection limit of the method was ∼0.1% (v/v). Improvement might be obtained with a stronger magnetic field [32] using, say, an 800 MHz machine, albeit at much higher cost.

On the other hand, the viscosity of the solution increases with [PMMA], and this leads to magnetic field inhomogeneity, even with a spinning sample. In addition, for a more viscous liquid, the spin-lattice (T_1) and spin–spin lattice relaxations (T_2) are short because of the decrease in molecular mobility. T_1 and T_2 have a pronounced effect on the widths of NMR spectral lines as they are directly related to the lifetime of a nuclear spin state: shorter relaxation time means more rapid reversion to a lower energy state. Thus, from Heisenberg's uncertainty principle, if a system exists in a given energy state for δt seconds, the uncertainty in the radiation frequency for that transition depends on the energy δE of that state and Planck's constant, h:

$$\delta v = \frac{\delta E}{h} \cong \frac{1}{2\pi\delta t} \tag{3}$$

For example, with $\delta t = 10^{-4}$ s (corresponding to a viscous liquid), $\delta v \approx 1000$ Hz, which leads to broad spectral lines and which thus requires a high-resolution instrument [33]. This effect may account for the poorer results for the most concentrated PMMA solution.

As indicated above, a goal was to identify a technique for routine use in the analysis of denture base PMMA for residual MMA. Factors to be considered included accessibility, costs, reliability and analysis time required. The time of analysis for both techniques was short (<∼10 min), but the detection limit for NMR appears to be slightly higher (>∼0.1%) than for GC (at most ∼0.004%); the cost of the deuterated solvent for the NMR was considerably higher than that of the dichloromethane. The machine cost and much greater complexity of operation of the NMR instrument are other factors to be considered. Overall, GC was deemed the better choice in the present context.

5. Conclusions

The GC analysis of MMA in PMMA by the direct injection of a solution in dichloromethane offers sufficient accuracy, with minimal cost and sample preparation. The results are compromised by neither solvent nor analyte losses during handling, nor by polymer decomposition at elevated temperatures. Furthermore, small samples can be used (of the order of 100 mg). This then is the preferred method for the routine analysis of the PMMA of denture bases.

Acknowledgements

We are grateful for the provision of facilities by the Department of Chemistry, The University of Hong Kong; for advice and support on NMR techniques from Dr. G.D. Brown, formerly lecturer of that department, and for technical assistance to Miss Bonnie Yam and Mr. Ho Kam Wing. This work was done in partial fulfilment of the requirements for the degree of Ph.D. by Christie Y.K. Lung at, and supported by a studentship from, the University of Hong Kong.

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