An investigation into the sample preparation procedure and analysis of cyanoacrylate adhesives using capillary electrophoresis

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Abstract

In this study, the trace acid profile of cyanoacrylate adhesives was studied using capillary electrophoresis. Liquid-liquid extraction was employed as the sample preparation step prior to separation by capillary electrophoresis. The solubility of the adhesives was investigated using various organic solvents, *e.g.* hexane and dichloromethane, and chloroform was determined to be the optimum solvent as it enabled the full dissolution of the adhesive. A comprehensive stability study was performed over a three-year period and results indicate that the adhesives were stable for two years after which their stability and performance degraded.

Keywords: A. Cyanoacrylate; D. Cure / hardening; Capillary electrophoresis;

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1. Introduction

Adhesives are defined as substances, which are capable of forming and maintaining a bond between surfaces. One such group of adhesives is the cyanoacrylates, which are commonly known as superglues [1]. Cyanoacrylates initially had limited success, which was attributed to two factors. Firstly, they were unstable during manufacture, and secondly, consumers were slow to recognise the advantages of these adhesives. These problems were addressed in the 1970s, with cyanoacrylates of exceptional adhesion being introduced [2]. They are now widely used both by consumers and in the automotive, electronics and furniture industries [3].

Cyanoacrylate adhesives are produced by a large scale condensation process. The alkyl cyanoacetate is condensed with formaldehyde in the reaction vessel. The resulting oligomers from this reaction are thermally depolymerised ("cracked"), leading to a crude monomer and a crack residue, which is discarded. The pure monomer is produced from the distillation of the crude monomer and the residue remaining from this distillation is recycled back into the reaction vessel to complete the production cycle. A flow chart providing a simple overview of the manufacturing process is illustrated in Fig. 1.

A number of inorganic and acidic anions may be present at different stages of the production process, such as nitrate and dialkyl phosphates (DAP), and in order to maintain the quality of the product, a sensitive and selective method for their quantification is required. The analysis of some of these anions has been performed using ion chromatography (IC) [4, 5] and recently capillary electrophoresis (CE) has emerged as a powerful analytical separation technique for the determination of small charged species, such as inorganic anions and organic acids [6-10]. It is an ideal method due to its low sample consumption and compared to chromatography methods, it results in rapid and highly efficient separations. As most inorganic anions exhibit very weak absorbance in the ultra-violet (UV) region, UV detection in the indirect mode was employed. Indirect UV detection was first introduced by Jones and Jandik [11, 12] for the determination of anions, and a number of background electrolytes have been employed, such as phthalate [13, 14] and chromate[12, 15]. Chromate is a highly

chromophoric species, and is ideally suited to the analysis of high mobility anions with high separation efficiencies (600,000 plates/m) achieved [16, 17].

In this investigation, the analysis of β-methoxyethyl cyanoacrylate adhesives was performed. The analysis of anions present in adhesive samples; however, can only be determined by CE if they are present in an aqueous solution. Therefore, a sample pre-treatment process was required. Extraction is the transfer of a solute from one phase to another and in this work liquid-liquid extraction (LLE) with chloroform was employed. The solubility of the adhesives was investigated using various organic solvents, *e.g.* hexane, dichloromethane, and chloroform and the optimum sample preparation method was determined. Using a developed CE method [18, 19] a comprehensive trace anion profile of the cyanoacrylate adhesives was generated, and results indicate that the adhesives were usable within a two-year time frame after which their stability and performance deteriorated.

2. Experimental

2.1 Chemicals

Chloroform (HPLC and Chromasolv grade). All other chemicals were of reagent grade. Sodium chromate, sodium hydroxide (NaOH), cetyltrimethylammonium bromide (CTAB), sodium sulphate, sodium nitrate, sodium dihydrogenphosphate, formic acid, diethyl phosphates (DEP), methacrylic acid, methyl sulphonic acid (MSA) and cyanoacetic acid were obtained from Sigma Aldrich (Tallaght, Dublin). Potassium chloride and potassium fluoride were obtained from Fluka (Buchs, Switzerland). Stock solutions of anions were prepared with deionised water from a Hydro Nanopure system to a specific resistance > 18MΩ-cm (Millipore, Bedford, MA, USA). Cyanoacrylate adhesive samples were obtained from Henkel Technologies (Irl.) Ltd.

2.2 Capillary electrophoresis instrumentation

All separations were performed on Beckman P/ACE MDQ instrument (Fullerton, CA), equipped with a UV absorbance detector. Detection was performed at 254 nm with a deuterium lamp. Data analysis was performed using Beckman (version 3.4) software. Polyimide-coated fused silica capillaries, (Composite Metal Services Ltd., England), 50 μm internal diameter (i.d.) were employed with an effective length of 0.50 m and a total length of 0.58 m.

2.3 Capillary electrophoresis procedures

All electrolyte solutions consisted of 15 mM chromate and 1mM CTAB. The pH of the electrolyte was adjusted to 8.5 using 1 mM sulphuric acid (H_2SO_4). All electrolyte solutions were filtered with 0.45 μm swinny filter (Gelman Nylon Acrodisc, 4438) prior to use. New capillaries were conditioned with methanol (MeOH), 1 M HCl, water, 0.1 M NaOH, water and background electrolyte (BGE) for 5, 10, 1, 20, 1 and 5 min. respectively. Before each analysis the capillary was rinsed for 1, 1 and 5 min. with MeOH, 0.1 M NaOH and BGE. Sample introduction was performed hydrodynamically, at 0.5 psi for 5 sec. Separations were performed with reversei polarity at 10 kV and the temperature was maintained at 25 °C.

2.4 Adhesive sample preparation

A 1 g quantity of the adhesive sample was dissolved in a 20 ml volume of chloroform and a 10 ml volume of the internal standard was added. The internal standard for the CE method employed was chloroacetic acid (pH =3.5, 50 μg ml^{-1}). The solution was mixed thoroughly and left to stand to allow complete separation of the two layers (*i.e.* the aqueous and organic layers). The upper aqueous layer was removed and filtered through a 0.45 μm swinny filter (Gelman Nylon Acrodisc, 4438) before analysis by CE. Three replicate extractions and a blank were performed for each sample and the % recovery of chloroacetic acid was obtained.

3. Results and discussion

3.1 Sample-preparation procedure

The cyanoacrylate production process is illustrated in detail in Figure 2. The condensation of the alkyl cyanoacetate with formaldehyde results in a prepolymer that by heating, is depolymerised ("cracked") into a liquid monomer (crude monomer). For the reaction to occur smoothly, the base catalyst is removed by the addition of appropriate acids (*e.g.* phosphoric acid, sulphuric acid). This monomer may be altered by modifying the –COOR group of the molecule to obtain compounds of different alcohol chain lengths. The crude monomer undergoes a purification process, *i.e.* a distillation, whereby impurity anions will be removed. This distillation results in the formation of a pure monomer. When applied as a thin layer between two appropriate substances, the pure monomer cures and forms strong bonds between surfaces by addition polymerisation initiated by adsorbed water. The addition of a free radical inhibitor, *e.g.* hydroquinone, prevents the monomer undergoing free radical induced repolymerisation on storage.

The anions expected to be present in the adhesive sample include chloride, sulphate and formic acid. In order to quantify these anions using CE, the adhesive sample must be aqueous. Therefore, a sample pre-treatment process required. In this study sample pre-treatment was performed by LLE. LLE is one of the most extensively studied sample preparation techniques due to its simplicity and convenience. In LLE, sample constituents are extracted into an aqueous phase from a water-immiscible organic phase. Organic solvents employed include diethyl ether, hexane and chloroform [20]. In this study, for the analysis of adhesives, LLE was performed using chloroform as the organic phase and the internal standard, chloroacetic acid as the aqueous layer. A blank LLE, *i.e.*, of chloroacetic acid, was performed in triplicate and from a known standard the % recovery of chloroacetic acid for each sample analysis was obtained, and are shown in Table 1. In this investigation, samples were taken from different stages of the β-methoxyethyl cyanoacrylate production process (*i.e.* crude monomer, distillation residue and pure monomer samples), and were analysed using CE. Typical electropherograms of β- methoxyethyl cyanoacrylate adhesive samples are illustrated in Fig. 3. The distillation of the crude monomer is a purification process that removes any

impurities and results in the production of the pure monomer. The two electropherograms in Fig. 3 illustrate the difference both quantitatively and qualitatively between the two stages of the production process, *i.e.* the crude monomer stage and the pure monomer production.

The crude monomer is expected to contain higher quantities of the analytes, chloride, sulphate and dimethoxyethyl phosphate, (DMEP), as this stage is prior to the purification step. Also, as the pure monomer is subjected to a distillation, the sample contains less analytes (DMEP is not present in the pure monomer, Fig. 3 and Table 2) and the absorbance response is lower for this sample. The concentration of chloride in the crude monomer sample was determined to be 31.3 μg ml^{-1} whereas in the pure monomer sample this has reduced to less than the limit of detection (1 μg ml^{-1}). There is a decrease, too in the amount of sulphate determined in the crude monomer sample to compared to the final pure monomer sample, *i.e.*, a reduction of 49% from the crude monomer sample to the pure monomer sample. This demonstrates the effectiveness of the distillation process stage in the removal of impurities from the adhesive.

The presence of chloride in the sample was initially thought to be due an artefact of sample pre-treatment. In order to investigate this, a range of solvents were employed to dissolve the cyanoacrylate sample, such as hexane, dichloromethane and toluene. However, none of these solvents provided satisfactory extractions and chloroform was employed for all extractions, as this was the only solvent, which enabled the full dissolution of the adhesives. The analysis of the adhesives was also performed using a higher grade of chloroform, (Chromasolv), and the % recoveries obtained for both grades of chloroform were comparable, 73-85%, with slightly reduced % relative standard deviation (RSD) values obtained with HPLC chloroform, Table 1.

The influence of Chromasolv chloroform on the concentration of chloride in the adhesive samples was investigated, Table 3. A decreased quantity of chloride was determined with the higher grade of chloroform for the distillation residue and crude monomer samples with no chloride detected in the pure monomer sample. For the distillation residue sample, this was as a direct result of a reduced % recovery, with a higher %RSD obtained with Chromasolv chloroform than the % recovery obtained

with the HPLC grade. It can also be concluded that the reduced quantity of chloride in the sample was due to the higher quality of chloroform in the sample pre-treatment.

3.2 Stability of cyanoacrylate adhesives

The optimum sample preparation procedure was applied to the analysis of cyanoacrylate adhesives. CE is an ideal method for their analysis, due to its low sample consumption and compared to chromatography methods, it results in rapid and highly efficient separations [21-23]. A CE method was developed, which was successfully applied to the quantification of inorganic and acidic anions present in cyanoacrylate adhesive samples [19]. The quantification of the anions and peak confirmation in the samples, were performed using both the internal standard method and by peak spiking.

The stability of the adhesive samples was investigated over a three-year period and Fig. 4 illustrates electropherograms obtained for the analysis of the β- methoxyethyl cyanoacrylate crude monomer sample within this time frame. From this it was apparent that firstly, the concentration of the analytes decreases from the first year of analysis, for example, the concentration of sulphate has decreased from 44.6μg ml^{-1} in year 1, to 12 μg ml^{-1} in the final year. It is also evident that there are extra unidentified peaks in the electropherogram, and that some analytes had been eliminated from the final year analysis, such as chloride, sulphate and cyanoacetic acid, in the crude and pure monomer samples. This suggests that the adhesive sample has destabilised over time, possibly due to the addition of the process acids during the production. From Fig. 5, it was determined that the acid MSA was generated over time (year 3). This was expected as the acid MSA is a by-product of extended storage over time.

From these investigations it was found that, using CE, the efficiency of the manufacturing method in the removal of impurities from the adhesive could be monitored. The ability of CE to effectively monitor the cyanoacrylate production process was illustrated. CE offers many advantages over chromatography techniques, such as reduced sample volumes required for analysis by CE (nanolitre, nl) compared to microlitre (μl) volumes required for IC. Also, the length of analysis with

CE was significantly reduced with CE, notably 15 min. for CE compared with 25 min. for IC [19]. Moreover, CE was shown to be suitable for the in-depth stability studies of the adhesives in question.

4. Conclusion

A simple and reproducible sample preparation method was developed and successfully applied to the analysis of cyanoacrylate adhesives. Chloroform was determined to be the optimum solvent for their analysis as it enabled full dissolution of the sample. A comparison was made between two grades of chloroform, HPLC and Chromasolv, and the optimum method developed with HPLC grade resulted in decreased % RSD values, <8 % and large % recoveries, 77-83%. The relationship between the type and concentration of the trace acids present in the cyanoacrylate adhesive and the stability and performance attributes of the adhesive may be monitored using CE. It is proposed that CE represents a powerful alternative to the traditional chromatographic technique for the simultaneous analysis of inorganic and acidic anions in a cyanoacrylate matrix. The efficiency of the production process was demonstrated. The effectiveness of the CE method in tracking the increasing purity of the cyanoacrylate ester as it passes through the various purification steps in the production process was clearly shown.

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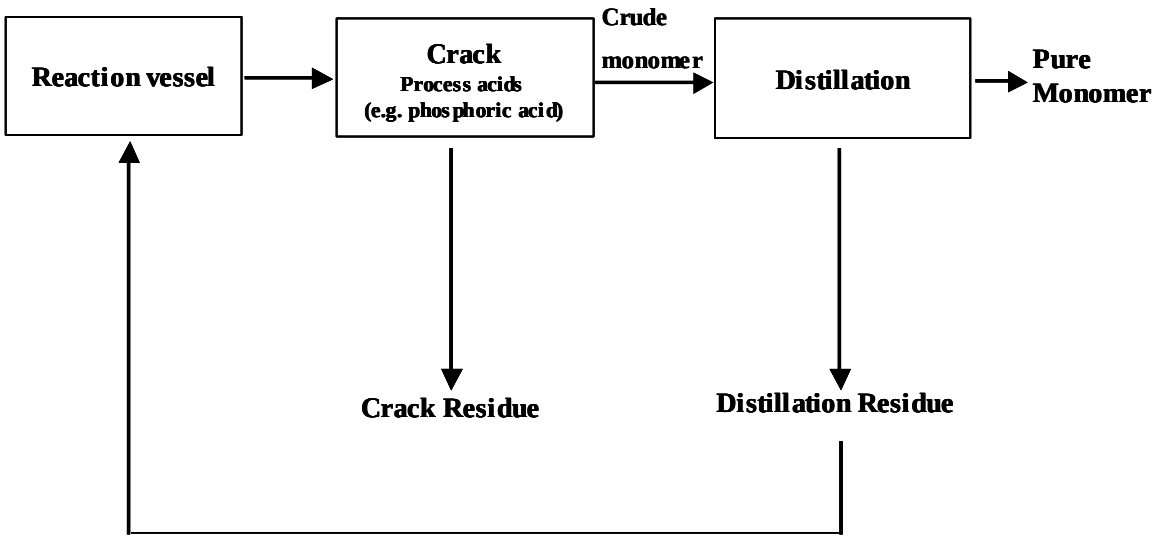
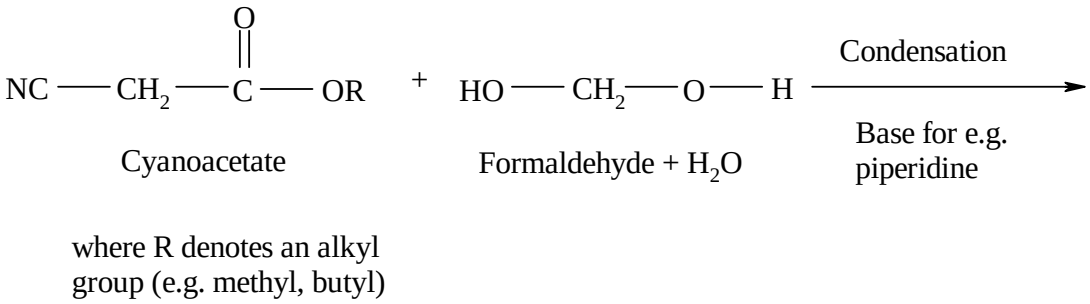
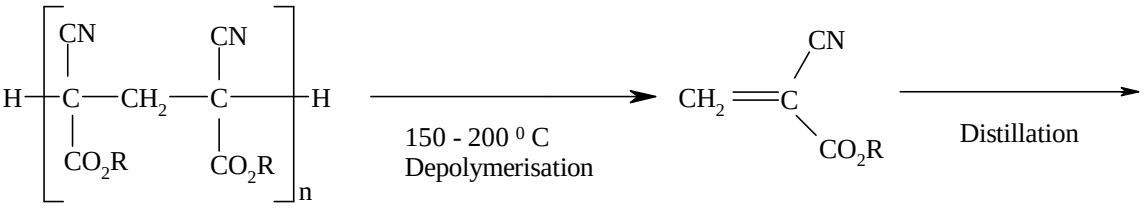


Fig. 1 The cyanoacrylate production process



where R denotes an alkyl group (e.g. methyl, butyl)



Pure monomer + Glutarate residue

Fig. 2 The cyanoacrylate manufacturing process

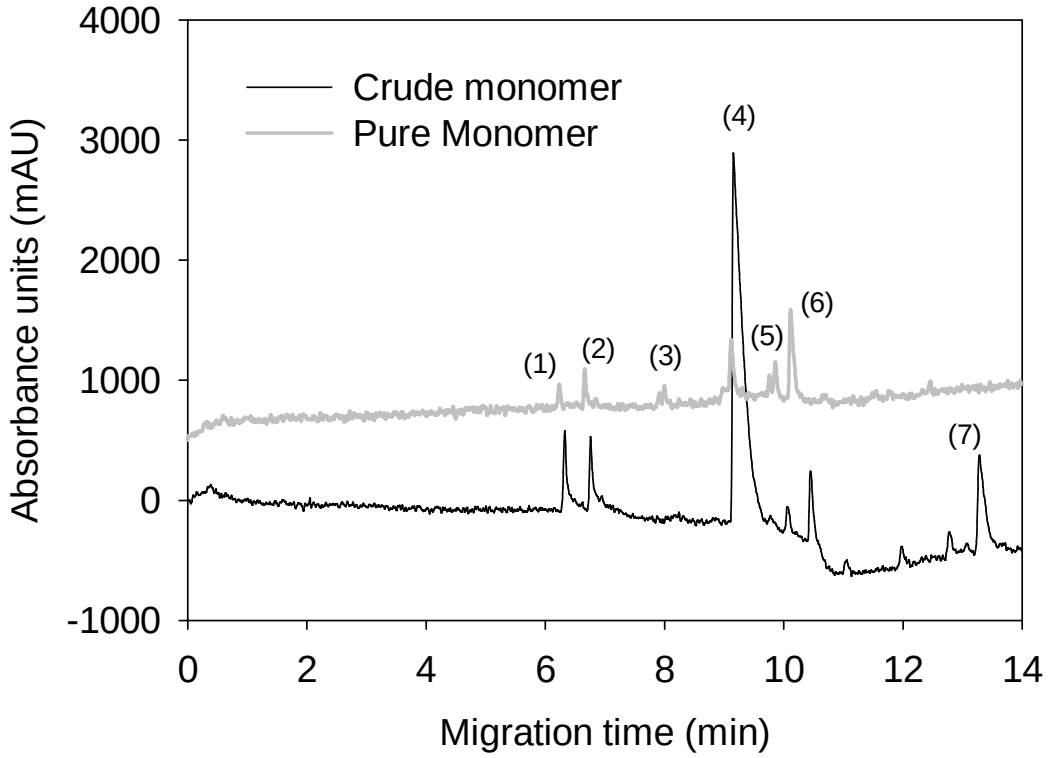


Fig. 3 Capillary electrophoresis analysis of β-methoxyethyl cyanoacrylate crude monomer and pure monomer samples. The components have been identified as follows (1) chloride, (2) sulphate, (3) formic acid (in pure monomer only, (5 μg ml $^{-1}$), (4) MSA, (5) cyanoacetic acid, (6) chloroacetic acid, internal standard, and (7) DMEP. Separation voltage -10 kV, pressure injection 0.5 psi / 5 s, with indirect UV detection at 254 nm. BGE: 15 mM chromate, 1 mM CTAB at pH 8.5. Separation temperature 25 $^{\circ}$C. Effective capillary length 0.50 m

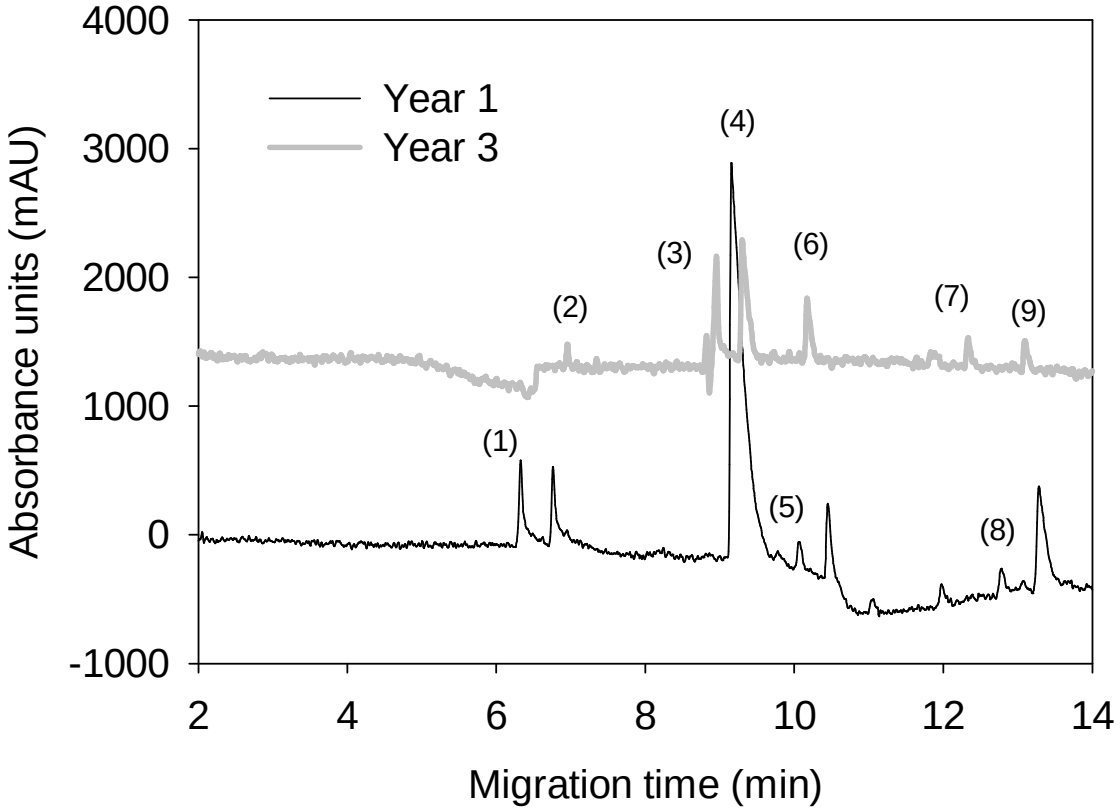


Fig. 4 Capillary electrophoresis analysis of a β-methoxyethyl cyanoacrylate crude monomer sample over a three-year period. The components have been identified as follows (1) chloride, (2) sulphate, (3) unidentified peak, (4) MSA, (5) cyanoacetic acid, (6) chloroacetic acid, internal standard, (7) unidentified peak, (8) unidentified peak and (9) DMEP. All operating conditions as in Fig. 3.

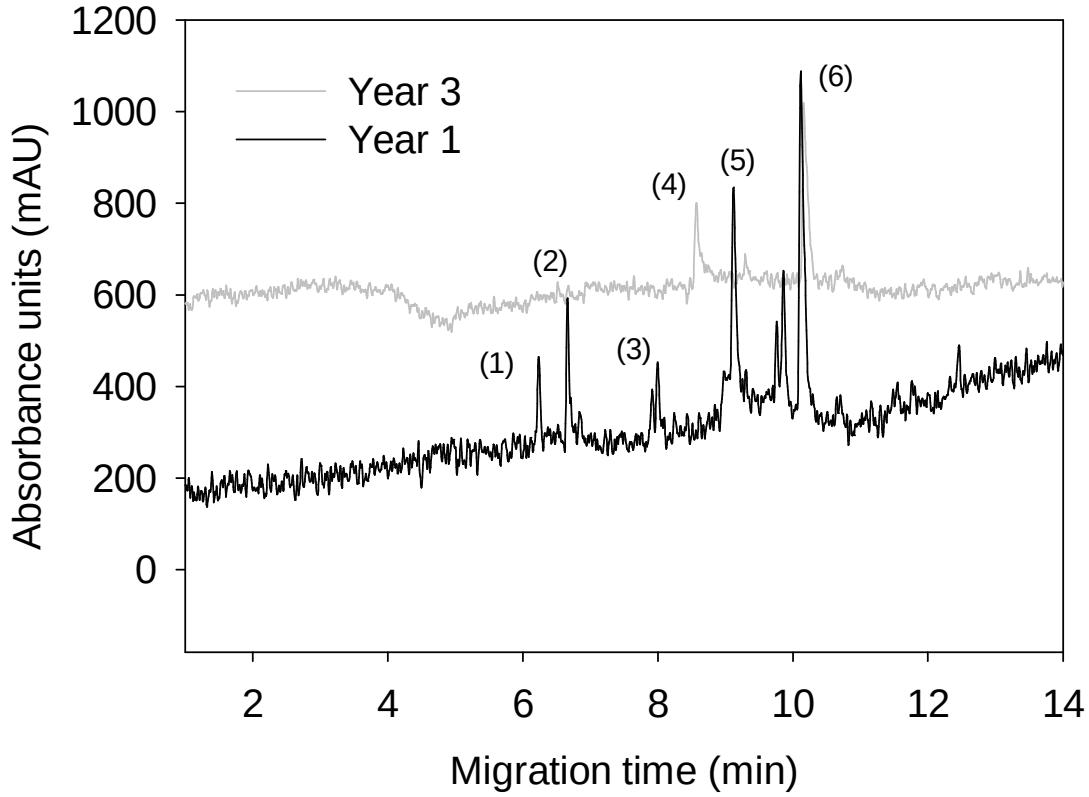


Fig. 5 Capillary electrophoresis analysis of a β-methoxyethyl cyanoacrylate pure monomer sample over a three-year period. The components have been identified as follows (1) chloride, (2) sulphate, (3) formic acid, (4) MSA, (5) cyanoacetic acid and (6) chloroacetic acid, internal standard. All operating conditions as in Fig. 3.

Table 1. *A comparison of the % recoveries and chloride concentrations determined for the ß methoxyethyl cyanoacrylate adhesive samples using HPLC and Chromasolv grade chloroform. Operating conditions as in Fig. 3*

Sample	% Recovery of chloroacetic acid HPLC Grade	% RSD (n=3) HPLC Grade	% Recovery chloroacetic acid Chromasolv Grade	% RSD (n=3) Chromasolv Grade
Crude monomer	77.3	4.4	73.4	4.9
Distillation residue	79.5	3.2	75.2	5.2
Pure monomer	84.2	1.8	85.7	2.6

Table 2. *Concentrations determined for some analytes for the ß methoxyethyl cyanoacrylate distillation residue. Operating conditions as in Fig. 3*

Sample	Analyte	Concentration (μg ml^{-1})	% RSD (n=3)
Crude monomer		31.3 ± 1.4	1.9
Distillation residue	Chloride	60.5 ± 12.0	19.9
Pure monomer		9.4 ± 1.1	12.1
Crude monomer		44.6 ± 3.7	8.3
Distillation residue	Sulphate	82.3 ± 3.0	3.7
Pure monomer		22.6 ± 1.5	6.6
Crude monomer		MSA	N/A
Distillation residue	MSA[a]	MSA	N/A
Pure monomer		22.5 ± 0.6	2.6
Crude monomer		11.3 ± 0.8	7.5
Distillation residue	Cyanoacetic acid	None detected	N/A
Pure monomer		None detected	N/A
Crude monomer		> 100	N/A
Distillation residue	DMEP	> 100	N/A
Pure monomer		None detected	N/A

Table 3. *Chloride concentrations determined for the ß methoxyethyl cyanoacrylate distillation residue with HPLC and Chromasolv grade chloroform. Operating conditions as in Fig. 3*

Sample	Concentration ($\mu g\ ml^{-1}$) HPLC Grade	Concentration ($\mu g\ ml^{-1}$) Chromasolv Grade
Crude monomer	31.3 ± 1.4	31.1 ± 1.4
Distillation residue	60.5 ± 3.4	49.8 ± 4.7
Pure monomer	9.4 ± 1.1	None detected