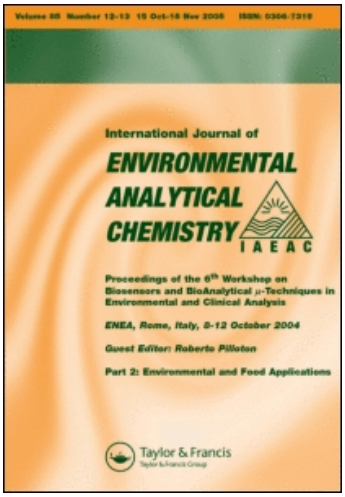

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Modern Analytical Techniques for the Detection of Rubber Chemicals and Their Decomposition Products in the Environment

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MODERN ANALYTICAL TECHNIQUES FOR THE DETECTION OF RUBBER CHEMICALS AND THEIR DECOMPOSITION PRODUCTS IN THE ENVIRONMENT

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Amine derived accelerators are decomposed during the vulcanisation of rubber and thereby may generate small quantities of nitrosamines. A method has been developed for monitoring nitrosomorpholine in vulcanisation fumes. The fumes are trapped in an absorbing solution and analysed by single ion monitoring GCMS. The method has been applied for both rubber vulcanisation presses and simulation devices. The presence of free volatile morpholine in certain accelerators may give rise to e.g. smell problems. Free morpholine in di-thio-bis-morpholine was determined by passing air through the powder sample and trapping in dilute HCI. The resulting solution was analysed directly by isotachophoresis. An HPLC method has been developed for the determination of p-phenylene diamine, a known skin irritant. The method has been applied on commercial p-phenylene diamine based rubber antidegradants.

KEY WORDS: Nitrosomorpholine, morpholine, GCMS, HPLC, isotachophoresis, rubber additives

INTRODUCTION

The chemical industry is constantly assessing the safety of its operations and the environmental fate of chemicals. In spite of close attention to prevention of spills and emissions, release to the environment may occur during production, with potentially deleterious effects on human health and the environment. Furthermore, man and the environment intentionally come in contact with products during use, and there is always the problem of chemicals and other products, which must be disposed of in an environmentally acceptable manner.

Industrial chemicals and their decomposition products are often very complex and require specialized methods of analysis. We will report here on some of the methods that we have developed and on how modern sensitive analytical techniques support efforts to ensure a safe and healthy workplace and a clean environment. The production and use of rubber chemicals will be used as an example.

During the production stage, air pollution and industrial hygiene at a manufacturing location and at the rubber processor's location are very important issues. Vulcanisation fumes have been investigated by single ion monitoring GCMS

(SIM-GCMS), one of the most sensitive analytical techniques available, to quantify low levels of nitrosomorpholine.

Chemicals normally do not contain harmful impurities however manufacturing and handling should be well controlled in the case that extemely low levels of contaminants may be present. Therefore we have developed several methods to monitor the levels of reaction by-products of our chemicals. Examples quoted are the analysis of specific impurities in paraphenylene diamine antidegradants and sulphur donors by HPLC and isotachophoresis.

DETERMINATION OF N-NITROSOMORPHOLINE IN RUBBER VULCANISATION FUMES

The Nitrosamine Issue in the Rubber Industry

Many N-nitrosamines have been shown to be animal carcinogens and, whilst there is no direct evidence that they are carcinogenic to man, it is obviously prudent to minimize exposure to these substances as much as possible. N-nitrosamines are formed by interaction of a secondary amine with nitrosating agents, e.g. oxides of nitrogen, nitrites and organic nitroso compounds.

Following the publication of a paper by J. M. Fajen *et al.*[1] and his further reports[2,3] which reported that N-nitrosamines had been found in a chemical plant which was manufacturing chemicals for tyre curing, and that N-nitrosomorpholine was found in an aircraft tyre factory atmosphere, we thought it of interest to study the conditions leading to the generation of N-nitrosomorpholine during the vulcanisation of rubber. This action has recently been re-emphasized following regulatory action in Germany.

Analytical Conditions

Instrumentation: Single ion monitoring GCMS has been used for the analysis of nitrosomorpholine. Two different GCMS instruments have been used for this work:

1) VG7070 EQ magnetic sector instrument; electron impact ionisation mode: 70 eV electron energy, 200 μA trap current, 6 kV accelerating voltage; detector: electron multiplier 3000 ev, amps full scale $10,^{7}$ gain multiplier 1, response time 10 ms; GC column: RSL Superox FA polyethylene glycol, length 50 m, i.d. 0.32 mm, df 0.3 μm; GC program: 90 °C for 4 minutes, rate: 5 °C/min, 160 °C for 5 minutes; carrier gas: helium at 2 ml/min; splitless injector at 120 °C, GCMS interface at 190 °C, MS source at 200 °C; volume injected: 1 μl.

2) Hewlett Packard 5985A quadrupole instrument; electron impact ionisation mode: 70 eV electron energy, 210 μA emission current, SIM cycle time: 200 ms; detector: electron multiplier 2800 or 3000 eV; GC column: FFAP glass capillary column, length 50 m, i.d. 0.5 mm; GC program: 150 °C for 2 minutes, rate:

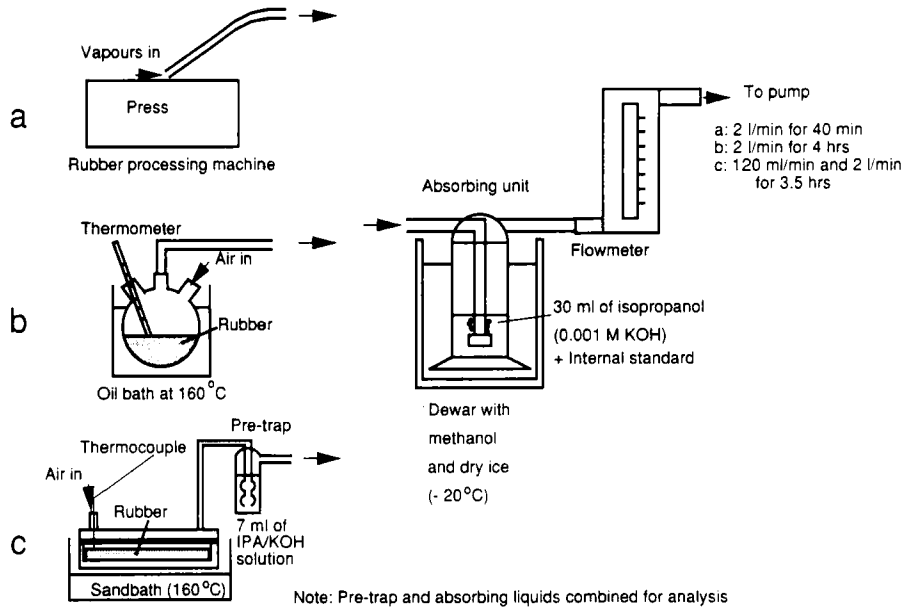


Figure 1 (A) Vapours from a rubber vulcanisation press. (B) Rubber vulcanisation simulation. (C) Vulcanisation press simultation.

8 °C/min, 180 °C for 5 minutes; carrier gas: helium at 8 ml/min; injector at 150 °C, GCMS interface at 275 °C, MS source at 200 °C; volume injected: 1 μl.

Sampling set-ups and simulation: Two different simulation experiments were carried out and compared with sampling at a rubber vulcanisation press. Experimental set-ups and details are shown in Figure 1.

Rubber compounds analysed: The base rubber compound (master-batch) used was as follows (expressed as parts per hundred of rubber, phr): Natural rubber (100 phr), carbon black (50 phr), oil (3 phr), zinc oxide (2 phr), stearic acid (5 phr). Sulphur, 2-morpholino-benzothiazole sulphide vulcanisation accelerator and dithio-bis-morpholine sulphur donor were added according to the amounts given in the text.

Results and Discussion

Before commencing any work to study the conditions which lead to generation of N-nitrosomorpholine during the rubber curing process, it was necessary to develop methods to carry out the analytical measurements of any N-nitrosomorpholine evolved either from the press or the simulation experiments. This was approached following the sequence: (i) development of a suitable analytical method for measuring N-nitrosomorpholine; and (ii) develop a suitable way of duplicating a curing operation in a closed system with collection of the vapours evolved.

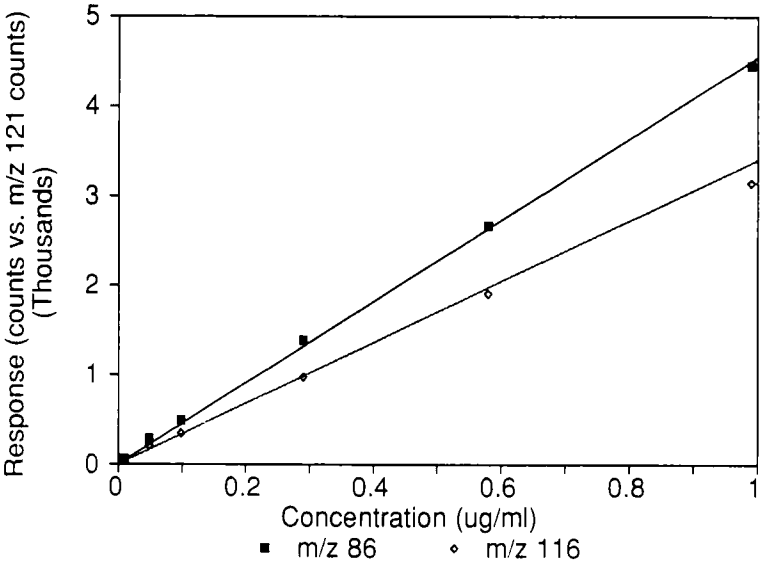


Figure 2 The SIM-GCMS calibration curves for N-nitrosomorpholine.

Analytical method development: The use of single ion monitoring GCMS, (also named specific ion recording) for the determination of volatile N-nitrosamines has been reported in the literature.[4] The conditions used are described in the experimental section and were validated in conjuction with the method recommended by Jiminez *et al.* for collecting nitrosamines in airborne samples.[5]

N-nitrosomorpholine in isopropanol solution was injected into the GC and the mass spectrum of the peak eluting was recorded in scan mode. three main ions were observed at m/z 116, 86 and 56, corresponding to the literature spectrum. A calibration curve was obtained by analysing standard solutions with N-nitrosomorpholine concentration varying over the range of 99.5 to 0.0098 μg/ml. Quantification was carried out by comparison of calculated peak areas at masses 86 and 116 for nitrosomorpholine standards versus samples. A typical calibration curve obtained on the VG 7070 EQ instrument is shown in Figure 2, indicating that the response was linear. Also from the results obtained it was estimated that the minimum detectable quantity was 10 picogram in a 1 μl injection. Similar results have been obtained on the Hewlett Packard 5985A instrument, however, with a higher detection limit of 180 pg in a 1 μl injection.

The simulation equipment used for the experiments was checked for collection efficiency of N-nitrosomorpholine. To test the glass flask method, 10 μg of N-nitrosomorpholine was introduced in the flask as a 0.1% solution in diethylether. For the stainless steel mould method, 50 μg was introduced as 1% solution in isopropanol. the collection efficiency experiments were carried out under identical gas flow and collection conditions as the experiments with rubber. The collection efficiencies were 86% (average of 3 experiments) for the glass flask and 130% for the stainless steel mould. In view of the experiments with rubber, we considered these collection efficiencies as satisfacory to continue the work.

Table 1 Comparison of results from press and simulation equipment: amounts of N-nitrosomorpholine generated

Compound: Masterbatch + 0.7 phr* 2-(4-morpholine)-benzothiazole sulphide (MBS) 0.5 phr dithio-bis-morpholine (DTBM) 1.5 phr sulphur (total morpholine: 0.61%)	
Press	*Laboratory flask*
20 min at 145 °C	4 hours at 110 °C
20 min cooling	
0.2 mg/kg	0.5 mg/kg

*phr: parts per hundred of rubber

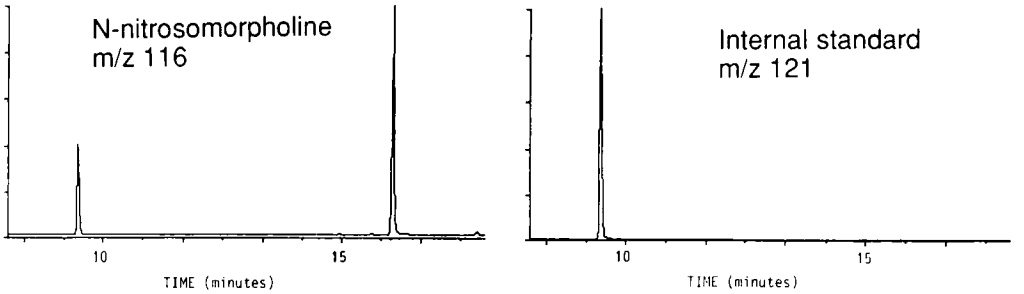


Figure 3 SIM-GCMS chromatograms for N-nitrosomorpholine and the internal standard (N, N-dimethyl aniline).

Results: The results for the quantification of N-nitrosomorpholine generated are expressed as milligrams formed per kilogram of rubber used. All measurements were made in duplicate and the average values are quoted. Table 1 shows a comparison of the different sampling and simulation techniques used. Figure 3 shows typical SIM chromatograms of a sample of rubber vulcanisation fumes.

Comparison of several press and laboratory flask experiments have shown that the laboratory flask experiment represents a worst case situation. Therefore, we tried to develop a more realistic simulation device. The conditions are also closer to the press conditions, i.e. presence of metal surfaces, better heat transfer etc. Preliminary experiments showed that 0.08 μg N-nitrosomorpholine was generated from a compound containing 1.5 phr MBS and 1.5 phr of sulphur.

Similar collection and analysis techniques have been applied successfully to monitor workplace air.

DETERMINATION OF FREE P-PHENYLENEDIAMINE IN PPD ANTIDEGRADANTS

Background

Para-phenylenediamine (1, 4-diaminobenzene, PPDA) is a known skin irritant. Its

basic structure is similar to N-alkyl para-phenylene diamine antidegradants (PPD's) and interest has been shown in its potential presence in products currently on the market.

A method, based on HPLC, has been developed to estimate trace levels of PPDA in PPD antidegradants and applied on N-Isopropyl p-phenylene diamine (IPPD) and N-1, 3-dimethylbutyl p-phenylene diamine (6PPD).

Experimental

HPLC method: The equipment used consisted of 2 Waters 6000A pumps, Waters WISP M710 autosampler, Waters M730 integrator, Waters M721 system controller, Waters 440 UV detector (fitted with 254 nm filter). A Lichrocart RP18 column (250 mm length, 4 mm i.d., 7 μm Lichrosorb RP 18 particles) was used throughout the study. HPLC eluents (all HPLC grade; methanol: Burden & Jackson, water: Lichrosolv, Merck) were: A: 20% methanol/80% water (v/v), 0.01 M ammonium acetate; B: 100% methanol; 0.01 ammonium acetate. The following solvent program was developed: 100% A for 5 minutes, linear gradient (curve 6) to 100% B in 10 minutes, 100% B for 10 minutes, 100% A for 10 minutes to re-equilibrate.

The PPDA was detected by UV at 254 nm; 0.005 AUFS was the typical sensitivity. Injection volumes applied were 20 μl (nominal volume on WISP autosampler). Peak heights were used for quantification.

Preparation of standards and sample solutions: approx. 10 mg of PPDA (Janssen Chimica, 97% purity) was accurately weighed and dissolved in 100 ml of methanol (Merck, p.a.). This stock solution was diluted by taking 2 ml and making up the volume to 50 ml with methanol. Standards were prepared from this dilution by taking resp. 1 and 2 ml and making up to 50 ml with methanol. Sample solutions of approx. 1% w/v were prepared by accurately weighing approx. 200 mg and dissolving in 20 ml of methanol. To accelerate dissolution an ultrasonic bath was applied for about 2 minutes.

Results and Discussion

A first attempt was made to analyse for PPDA by capillary gas chromatography. However, during the tests it became apparent that the GC method suffers from a number of drawbacks:

1) the peakshape of PPDA is far from ideal, even on a polar column (polyethylene glycol wax);

2) PPDA is well separated from other impurities on a non-polar column (polydimethylsiloxane) but interferences occur on more polar phases (polymethylphenylsiloxane or polyethylene glycol wax);

3) the detection limit that can be reached by FID detection was not sufficient to attain a 5 ppm detection limit in the antidegradants which was required.

Table 2 PPD's analysed and ppda levels

Sample[a]	*ppda (ppm)*
N-Isopropyl p-phenylene diamine (1)	<2
N-Isopropyl p-phenylene diamine (2)	<2
N-1, 3-dimethylbutyl p-phenylene diamine (1)	<2
N-1, 3-dimethylbutyl p-phenylene diamine (2)	<2

[a]Products from two different manufacturers (1) and (2) have been analysed.

GCMS could be used to improve specificity and detection limits, but it does not cope with the poor chromatographic performance.

HPLC was therefore examined as a potential alternative.[6] After several trials it was found that PPDA could be separated from other highly polar impurities by an isocratic analysis with a 20% methanol/80% water eluent. Ammonium acetate (NH_4Ac, 0.01 M) was added as a buffer. After an initial isocratic period, a gradient to 100% methanol was run to flush out all other compounds, such as the PPD's.

The PPDA was detected by UV at 254 nm. This is not at the maximum absorbance, but is sufficiently sensitive to obtain a 0.4 ng absolute detection limit. Use of 240 nm absorbance or an electrochemical detector might further decrease the detection limit. From two standard solutions, with concentrations of 0.093 ppm and 0.186 ppm (weight/volume) respectively and the noise level, the detection limit (2 × noise) was estimated at 0.02 ppm. This corresponds to 2 ppm of PPDA in a 1% (w/v) PPD solution.

Four samples have been analysed (Table 2). PPDA levels are below detection limit for all four products. A chromatogram of an IPPD sample is shown in

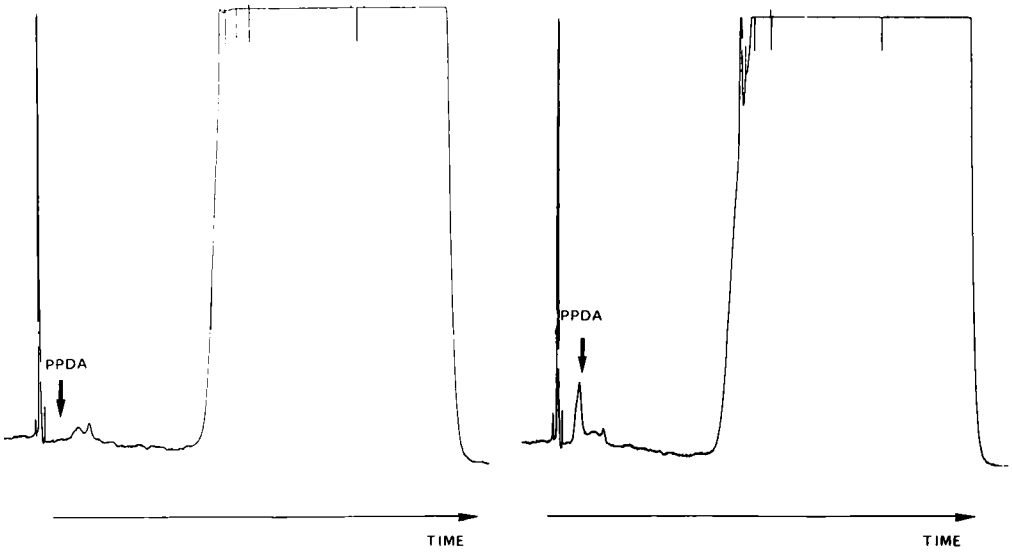


Figure 4 HPLC chromatograms of: (A) IPPD solution. (B) IPPD solution, spiked with P-Phenylene diamine.

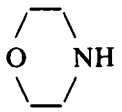
Figure 4a. Figure 4b shows IPPD spiked with PPDA and indicates the precise retention time if PPDA would have been present.

FREE MORPHOLINE IN DITHIO BIS-MORPHOLINE SULPHUR DONOR

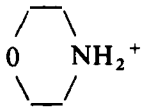
Background

Morpholine is a known skin irritant. Its presence in dithio-bis-morpholine (DTBM) may be a cause of irritation when handling dithio-bis-morpholine and chemically similar products.

Morpholine can be present either as free morpholine (I) or as the morpholinium ion (II). In the latter case, a counter anion, such as chloride or morpholino-sulphamate, has also to be present.[7]



(1)



(2)

Free morpholine will be volatile and therefore give rise to odour. The morpholinium ion is not volatile and should therefore not give rise to problems. The analytical procedure should take this difference into account.

Methods have been developed within our organisation to determine the total morpholine content of DTBM. Most of these methods use water extraction at some stage of the procedure, which will extract the total morpholine. The difference between volatile and non-volatile morpholine species is then lost.

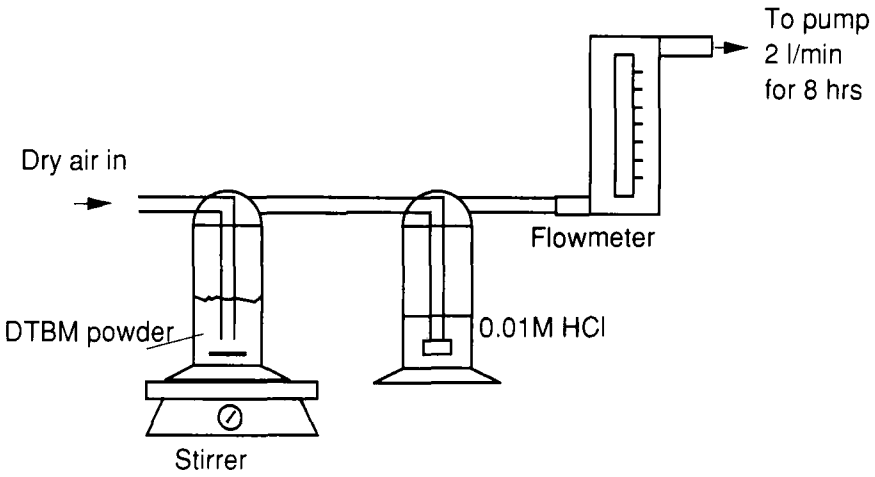


Figure 5 Experimental set-up for collection of morpholine vapours from DTBM.

Therefore, a method aimed at estimating the level of volatile morpholine was developed, based on the principles applied by Sollenberg and Hansén.[8]

Experimental

Sampling and collection of free morpholine: A drawing of the experimental set-up is given in Figure 5. The air pumped through at 2 litres/min was dried over a silica gel column before passing the DTBM to avoid hydrolysis of the sample. The trapping HCl solution (0.01 M) was made up to 40 ml after the experiment in order to restore the initial volume. This solution was analysed by isotachophoresis (ITP) without further treatment.

Water extracts of DTBM: approx. 5 grams of DTBM were extracted with 20 ml of water for 1 hour in an ultrasonic bath. The mixture was then centrifuged to separate solids and extract. The extract was filtered before analysis. It was analysed as such by ITP and after 1:10 dilution by ion chromatography.

Isotachophoresis conditions: A Shimadzu IP-2A isotachophoretic analyser, equipped with potential gradient detector, was used. Leading electrolyte: 0.005 M K^+, acetate counter ion to pH 5.5, 0.1% Triton X-100; Terminal electrolyte: 0.005 M n-aminohexanoic acid, acetate to pH 5; Capillary: 1st stage: 40 × 1 mm i.d., 2nd stage: 100 mm + 0.5 mm i.d.; Current program: 1st stage: 150 μA for 3 minutes, 2nd stage (detection): 75 μA; Temperature: 15 °C; Determinations were made using external morpholine standards.

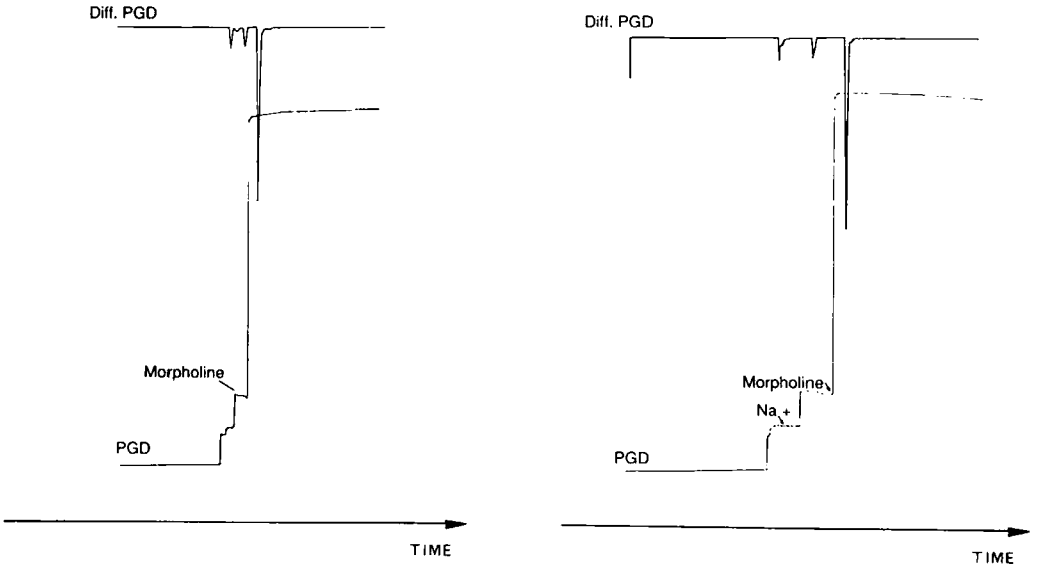


Figure 6 Isotachophoresis trace of cations present in: (A) The absorption solution of the morpholine vapours from DTBM. (B) The aqueous extract of DTBM.

Ion chromatography conditions: A Dionex Model 16, equipped with micromembrane suppressor and conductivity detector, was used. Column: Dionex AS1 anion separator column, with Dionex AG1 precolumn; Eluent: 2.4 mM Na_2CO_3 + 3 mM $NaHCO_3$; Flow: 2.3 ml/minute; Determinations were made using external chloride and sulphate standards. No standard of morpholinosulphamic acid was available. A response factor was estimated from older chromatograms.

Results and Discussion

Free (volatile) morpholine was determined in DTBM by passing air through powder samples for 8 hours and collecting the volatilised amine in dilute HCI. The resulting HCI solution was analysed by isotachophoresis for morpholine. Figure 6 shows the isotachogram of a typical vapour sample. Water extracts were also analysed for morpholine and morpholinium ion and sodium ion content by isotachophoresis (Figure 6b) and for the counter ions (chloride, morpholinosulphamate and sulphate) by ion chromatography (Figure 7). The balance between the cations (morpholinium) and the anions should confirm the content of free morpholine, i.e. not balanced by an anion.

As can be seen from the results in Table 3, the level of free morpholine is very low. Most of the morpholine is present as morpholinium ion with chloride and morpholinosulphate as counter ions.

CONCLUSION

Several methods for determining rubber chemicals, their decomposition products arising from vulcanisation and their impurities in environmental matrices have been developed. The use of laboratory simulations has shown to be extremely

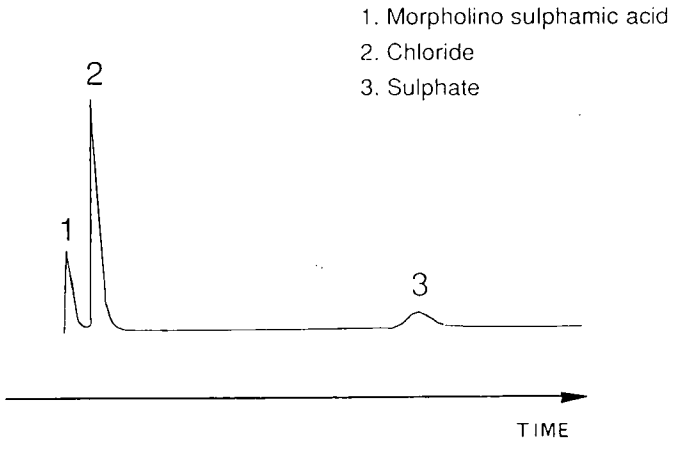


Figure 7 Ion chromatogram of anions present in the aqueous extract of DTBM.

Table 3 Morpholine species content of dithio dimorpholine

	% *free*[a]	% *total*[b]	% *Na*	% Cl^-	% *MSA*	% SO_4^{2-}
Old DTDM	0.023	0.275	0.000	0.072	0.144	0.018
New DTDM	0.007	0.096	0.022	0.030	0.023	0.018

[a]free: volatile free morpholine;
[b]total: morpholine + morpholinium ions

valuable to evaluate the potential impact rubber chemicals, rubber manufacturing and the use of rubber on the environment and human health.

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