Pergamon

Cement and Concrete Research 29 (1999) 899–907

CEMENT AND CONCRETE RESEARCH

Determination of durability-enhancing admixtures in concrete by thermal desorption and pyrolysis gas chromatography-mass spectrometry

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Manuscript received 8 December 1998; accepted manuscript 1 March 1999

Abstract

Two methods involving thermal desorption and pyrolysis gas chromatography-mass spectrometry are described for the determination of two durability-enhancing admixtures, a corrosion inhibitor and a shrinkage reducing agent (SRA) in hardened portland cement mortar and concrete. The corrosion inhibitor, based on calcium nitrite, is selectively measured by the in situ pyrolytic conversion of 2-aminobiphenyl to 2-phenylphenol. The SRA, which consists of a mixture of isomeric glycol and ether compounds, can be thermally desorbed directly from powdered concrete. For both durability-enhancing agents, the recovery rate generally exceeds 93% with no interference evident from several common chemical admixtures. Cement composition does not appear to significantly affect desorption efficiency for the SRA additive. Thermal desorption and pyrolysis gas chromatography are shown to be rapid, selective, and highly convenient methods for both qualitative and quantitative estimates of two important chemical admixtures.

Keywords: Durability; Corrosion; Admixture; Characterization; Shrinkage

In order to improve the resistance of concrete to various harmful agents and exposure conditions, several classes of durability-enhancing additives have been developed by manufacturers of chemical admixtures. Two especially important admixtures for preventing concrete deterioration are corrosion inhibitors [1] and shrinkage reducing agents (SRA) [2].

One of the established methods for reducing the corrosive action of chloride salts in concrete is the use of calcium nitrite [$Ca(NO_2)_2$]-based corrosion inhibitors [3]. The corrosion protection provided by $Ca(NO_2)_2$ occurs through its ability to restore defects (present as ferrous oxide) in the iron oxide layer at the steel surface [4], as shown in Eq. (1):

$$2\ Fe^{2+} + 2\ OH^- + 2\ NO_2^- \rightarrow 2\ NO + Fe_2O_3 + H_2O \qquad (1)$$

This redox reaction prevents the formation of expansive corrosion products, which in turn can cause cracking within the concrete. The amount of $Ca(NO_2)_2$ required to prevent corrosion of steel reinforcement is usually based on the anticipated level of chloride penetration into the concrete [5].

The SRA considered under this study consists of a mixture of glycol and ether isomeric compounds, and has been reported to be effective in providing long-term drying shrinkage reductions up to 50%, along with significant improvement in restrained shrinkage performance [6]. The primary mechanism by which SRAs reduce the strains and resulting stresses associated with rapid moisture loss of concrete has been proposed to involve a reduction of the surface tension of the pore water solution, which in turn is theorized to lower capillary tension forces [2].

Considering the critical benefits that $Ca(NO_2)_2$ and the glycol-ether blend can have on concrete durability, many users may desire verification that the amount of durability-enhancing admixture present in the concrete is consistent with the specified dosage. Various means of checking addition rates include: (a) actually monitoring the operation of the dispensing equipment as the admixture is added during the batching process; (b) checking the inventory of admixture in the concrete producer's storage tanks during daily concrete production; and (c) measuring the admixture content in the concrete either in the plastic or hardened state.

A method for measuring nitrite in hardened concrete has previously been reported whereby a pulverized portion is triply extracted with water, followed by either polarography, ion chromatography, or spectrophotometry to quantitate the extracted nitrite [7]. While the recovery rates from the extraction procedure were reported to normally exceed 90% of the originally added calcium nitrite for selected concrete mix designs, recommendations were also provided for

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PII: S0008-8846(99)00062-9

concrete mixtures when less than 85% of the intended dosage rate was measured. For these cases, actual job materials would have to be acquired for the preparation of lab concrete standards. The recovery rate from these standards would then be applied to the concrete under consideration.

No methods have been reported for either the qualitative or quantitative determination of glycol ether blends in concrete.

Recently, several reports have found combined instrumental methods, such as pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS), to be applicable for the determination of certain grinding aids in cement and chemical admixtures in concrete [8–12]. Incorporating a derivatization reaction within the pyrolysis process can greatly improve the volatility of tightly bound and nonvolatile additives in both cement and concrete, which facilitates their thermal desorption directly into the inlet of GC/MS instrumentation for subsequent identification and quantitative analysis. The potential advantages of Py-GC/MS over conventional solvent extraction-spectrometric methods include: (a) consistent and near complete recovery of the admixture independent of concrete mix design; (b) sufficient sensitivity to detect a wide range of additives normally present from 5 to 1000 ppm; (c) improved selectivity as provided by the chromatographic separation and mass spectral detection of thermally desorbed compounds; (d) considerably reduced analysis time and effort, thus improving productivity; and (e) the near elimination of solvent handling.

Several applications of Py-GC/MS for detecting durability enhancing agents in concrete have been previously evaluated. In the case of $Ca(NO_2)_2$, a pulverized portion of concrete was first treated with ammonium polyphosphate and then pyrolyzed at 800°C to convert the nitrite primarily to dinitrogen oxide (N_2O) along with a minor amount of nitric oxide (NO) [11]. While the results were limited to qualitative measurement of the nitrite, quantitative results may be possible if the pyrolytic acid decomposition step is found to produce a constant ratio of N_2O/NO. Py-GC/MS has also been applied to the determination of surface-applied organosilanes that are used as waterproofing agents for concrete [13]. Ballistic (instantaneous) pyrolysis at 700°C reportedly permitted quantitative measurement of alkyltriethoxysilanes in concrete sampled at various depths from the surface.

Previously reported GC methods for nitrite determination have involved various reaction schemes to form volatile derivatives: (a) diazotization with a volatile primary aromatic amine, which is then extracted into an organic solvent prior to GC analysis [14–18]; (b) diazotization followed by silylation to enhance volatility of the diazo derivative [19]; (c) oxidation of nitrite to nitrate, which is then reacted with 2,4-xylenol to form 6-nitro-2,4-xylenol [20]; and (d) oxidation of iodide in the presence of acetone to form monoiodoacetone [21].

In this study, the use of pyrolysis (Py) and thermal desorption (TD)-GC-MS are evaluated as viable methods for the quantitative determination of the $Ca(NO_2)_2$-based corrosion inhibitor and glycol-ether blend SRA in concrete, respectively. A specific objective was to understand the capability of derivatization coupled with heat energy to thermally extract >90% of admixed nitrite independent of the composition of the concrete mix design. For $Ca(NO_2)_2$, a derivatization procedure was developed based on the method reported by Jain et al.[14], who measured nitrite in water by acidifying the sample to produce nitrous acid. After the nitrosation reaction between nitrous acid and a primary amine such as 2-aminobiphenyl (2-AB), the diazonium reaction product was hydrolyzed to form 2-phenylphenol (2-PP), which was then extracted in hexane to remove impurities prior to GC analysis. In the case of nitrite content in concrete, treatment of a powdered sample with a solution of 2-AB in mild sulfuric acid followed by pyrolysis was found to quantitatively produce 2-PP, which was then analyzed by GC-MS.

In the present study, the coupling of py-GC-MS with the 2-AB diazotization procedure for measuring nitrite content was chosen because of the following factors: (a) diazotization and hydrolysis are performed with a single reagent, and the pyrolysis step can drive the hydrolysis reaction and thermal desorption of 2-PP from the concrete; (b) limited access to the amine group within the 2-AB reagent limits any self-coupling (self-reaction), but does not hinder hydrolysis at elevated temperatures to form 2-PP; (c) known interferences are limited to sulfide, iodide, copper II, and possibly phenol; and (d) the common solvent extraction step for minimizing interferences for diazotized nitrite in relatively complex matrices is eliminated by thermal extraction and selective mass detection.

The two-step reaction process, after the concrete is treated with mild sulfuric acid, H_2SO_4, to convert the nitrite to nitrous acid, HNO_2, is shown in Fig. 1.

In the case of the volatile compounds found in the glycol-ether blend, a range of ballistic and ramping thermal processes were explored to allow direct analysis of the concrete without pretreatment. As an independent verification of the glycol ether blend content in various mortar mixtures, several solvent extraction methods coupled with GC-MS analysis were attempted. The effect of cement brand and

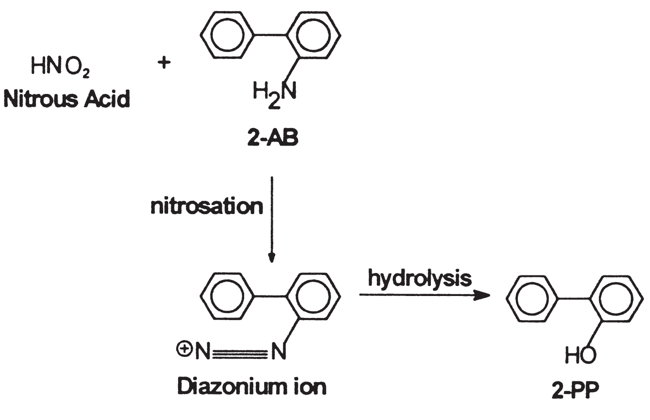

Fig. 1. Conversion of 2-AB reagent to form 2-PP.

presence of other admixtures on the determination of both nitrite and the glycol-ether blend by Py and TD-GC/MS were also evaluated. The inherent volatile nature of the compounds comprising the glycol-ether blend underscores the applicability of GC-MS as a viable means for analyzing the SRA admixture after thermal desorption from mortar and concrete. Gas chromatographic capillary columns using polyethylene glycol stationary phase have been reported as a common choice for glycol blends [22,23].

1. Experimental program

1.1. Preparation of concrete and mortar standards

The feasibility of measuring $Ca(NO_2)_2$ content by Py-GC/MS was initially evaluated using four 0.04 m^3 lab-prepared concrete mixtures (Table 1), prepared according to the procedure specified in ASTM C 192 Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory [24]. The $Ca(NO_2)_2$, formulated as a 30% solution, was added with the mix water at dosages equivalent to 0, 4.9, 14.8, and 26.7 L/m^3. Concrete cylinders, 100-mm diameter × 200-mm length, were cast and cured for 7 days at 22°C and 100% relative humidity. A 40-mm thick slice was cut longitudinally from the center of the cylinder, oven dried for 24 hours at 105°C, and then crushed until the entire concrete slice passed through a 300 μm sieve.

The reference standards used to measure the percent recovery of the admixed $Ca(NO_2)_2$ were prepared by adding various dilute solutions of $Ca(NO_2)_2$ to a portion of powdered control concrete. These slurries were then allowed to dry at ambient (22°C) temperature. This method of standardization essentially eliminates any bias that could result from adsorption of the nitrite by the paste fraction of the concrete, yet subjects the nitrite standards to the same test protocol used for the admixed $Ca(NO_2)_2$ concrete mixtures.

Once test conditions were optimized with the lab-prepared concrete mixtures, a series of 3-m^3 loads of ready-mix truck concrete were prepared with four addition rates of $Ca(NO_2)_2$-based corrosion inhibitor (Table 2). Cylinders were cast and the concrete was analyzed at an age of 1 week. A check on possible interference from other admixtures was performed by intergrinding a powdered concrete standard containing 4.9 L/m^3 $Ca(NO_2)_2$ with other concretes admixed with calcium lignosulfonate (lignin), corn syrup, naphthalene sulfonate formaldehyde condensate (NSFC), and triethanolamine (TEA).

Table 1
Mix design for lab-prepared $Ca(NO_2)_2$ concrete standards

	Mix proportions (kg/m^3)	$Ca(NO_2)_2$* addition rates (L/m^3)
Cement	365	Control
Sand	790	4.9
Stone	1038	14.8
Water	197	26.7
Unit weight	2385	

* 30% solution of calcium nitrite. SG = 1.30.

Table 2
Mix design for commercial-ready mix concrete

	Mix proportions	$Ca(NO_2)_2$[a] addition rates (L/m^3)
Cement	348 kg/m^3	7.4
Fly ash	57 kg/m^3	12.4
Sand	749 kg/m^3	17.3
Stone	1010 kg/m^3	22.2
Water	94 kg/m^3	
HRWR[b]	2.7 L/m^3	
AEA[c]	0.2 L/m^3	
Unit weight	2291 kg/m^3	

[a] 30% solution of calcium nitrite.
[b] Tall oil-based air-entraining agent.
[c] Lignin/NSFC-based high-range water reducer.

For the glycol-ether blend, mortar mixtures were prepared according to the proportions reported in Table 3. Mortar samples consisting of 75-mm diameter × 150-mm length cylinders were cast, cured for 7 days and crushed for analysis similar to the procedure used for the $Ca(NO_2)_2$ concrete standards.

The composition of the cements used to prepare both the laboratory concrete and mortar mixtures is reported in Table 4.

Initial Py-GC/MS experiments found that the concentration of both the $Ca(NO_2)_2$ and glycol-ether blend thermally extracted from their corresponding concrete and mortar mixtures were found to exceed the capacity of the mass spectral detection system. Subsequently, a tenfold dilution was performed on all samples by intergrinding a 2-g portion of the pulverized concrete or mortar with 18 g of the corresponding control mortar or concrete standards using a SPEX 8000 Mixer/Mill (Spex Industries, Edison, NJ, USA).

1.2. Thermal gas chromatography-mass spectrometry instrumentation

The instrumentation used for the TD and PY-GC/MS experiments consisted of a CDS 2000 Pyrolyzer (CDS Analytical, Oxford, PA, U.S.A.) operated in tandem with a Hewlett-Packard (HP) 5890 gas chromatograph (GC) equipped with an HP 5972A mass selective detector (MSD). The CDS 2000 pyroprobe, which includes a coiled platinum element

Table 3
Composition of SRA mortar mixes

	Mix proportion	Glycol-ether blend (ppm)
Cement (#133), g	2000	Control
Sand, g	4500	1300
Water, g	940	2600
		5200*
		7800

* Additional mortar mixtures were also prepared with cements #143, #170, #051, and #017, along with mortar containing the #133 cement and 1500 ppm of an NSFC-type superplasticizer.

Table 4
Composition of cements used for lab concrete and mortar mixtures (% mass)

Cement code	#133	#170	#051	#143	#017
ASTM C150 designation	T-I	T-I	T-I/II	T-I	T-II
SiO_2	21.06	21.39	20.62	21.13	20.56
Al_2O_3	4.51	5.00	4.34	4.93	3.92
Fe_2O_3	3.96	3.59	3.33	1.95	3.72
CaO	64.05	63.86	62.77	64.57	61.76
MgO	1.01	2.87	3.12	2.87	3.82
SO_3	2.59	2.39	3.67	2.52	2.56
Na_2O	0.19	0.04	0.23	0.08	0.37
K_2O	0.65	0.70	0.53	0.08	0.36
LOI	1.22	1.08	0.90	1.42	2.14
Alkalies as Na_2O	0.61	0.50	0.58	0.13	0.61
Free CaO	0.38	0.47	0.10	0.81	1.71
Bogue compounds					
C_3S	55	59	52	56	55
C_2S	19	13	20	18	18
C_3A	6	8	7	11	5
C_4AF	12	11	10	6	11
Blaine surface area (cm^2/g)	4000	3680	4090	3990	4590

where sample heating occurs, was interfaced with the GC injection port using a heated CDS 1500 Valved Interface. The temperature- and time-programming capability of the pyroprobe provided for flexible heating rates up to a final temperature of 1400°C. The platinum-coiled element allowed the use of quartz tubes (15-mm length × 6-mm diameter) that can hold up to 70 mg of powder after gentle tapping.

Upon heating the concrete and mortar, the thermally desorbed glycol-ether blend and 2-PP (the derivatized nitrite product) were immediately trapped at the inlet of a 30 m × 0.25 mm capillary column held at 35°C for the duration of the thermal desorption or pyrolysis processes. For the nitrite determination, the 2-PP reaction product was chromatographed on an Alltech Econo-Cap SE-54 column, while an HP-INNOWAX (crosslinked polyethylene glycol) column was used for the glycol-ether blend. The stationary phase of both columns had a 0.25 μm film thickness of stationary phase. In both cases, a 100:1 split ratio was maintained at the injection port, and the GC column temperature was programmed at 10°C/min to a final temperature of 280°C with the eluted compounds detected by MSD. The capability to obtain mass spectra on the eluted compounds was found to be quite useful for identifying both thermally desorbed compounds and pyrolysis products produced from heating the concrete and mortar samples to various temperatures. In the case of nitrite determination, the MSD was operated in the single ion-monitoring mode (SIM) at mass 170 to minimize background interference and improve precision.

1.3. Derivatization and thermal desorption methods

The pyrolytic reaction of nitrite with the 2-AB reagent and the subsequent thermal desorption of both the 2-PP reaction product and the glycol-ether blend were accomplished by packing 50 mg of the powdered concrete or mortar into the quartz tubes with small amounts of quartz wool inserted at the ends of the tube to prevent sample blowout. Various heating programs were applied to the pyroprobe to achieve maximum and consistent thermal extraction of the admixtures from the concrete and mortar. These included both ballistic heating (instantaneous temperature increase) up to 900°C coupled with variable hold times at final temperature, and temperature ramping starting at 200°C and applying a range of heating rates (120 to 600°C/min) to a final temperature of 900°C.

In the case of the nitrite measurement, consistent and maximum recovery rates were achieved by initially mixing 1 g of powdered concrete with 3 mL of a 0.50 M H_2SO_4 solution containing 0.5% 2-AB. After the mixture was allowed to dry at ambient temperature, 50 mg was then loosely packed in the quartz pyrolysis tube. Upon heating, thermal hydrolysis of the diazo intermediate occurs producing 2-PP and nitrogen gas, N_2. 2-PP is subsequently desorbed from the concrete and analyzed by GC-MS. The complete thermal desorption and pyrolysis variables examined in this study are listed in Table 5.

2. Results

2.1. Nitrite determination

2.1.1. Optimizing test parameters

Since the diazotization reaction requires conversion of nitrite to nitrous acid (HNO_2), care was required for selection of reagent volume and acid strength (M H_2SO_4) to fully wet 1 g of powdered sample and acidify the mixture to a pH of 2. Lowering the pH of concrete below pH 2 could cause the relatively unstable nitrous acid, HNO_2 (pKa = 3.4) to decompose to nitrogen dioxide, NO_2. Treatment of 1 g of concrete with 3 mL of a 0.50 M solution of H_2SO_4 was found sufficient to acidify the concrete to a pH of 2, thus converting the nitrite to nitrous acid.

In order to assure that sufficient 2-AB reagent was available to react with all the nitrite, a wide range of reagent concentrations, corresponding to 2-AB/nitrite mole ratios of 1.1, 2.1, 4.0, 6.9, and 8.1, were evaluated using a concrete standard admixed with 26.7 L/m^3 of a 30% solution of $Ca(NO_2)_2$. Detector response for 2-PP was found to reach a

Table 5
Derivatization-thermal desorption variables for nitrite and SRA content in concrete

Parameter	Range
Desorption temperature	300–900°C
Heating rate	Ballistic; 120–600°C/min
Hold time at final desorption temperature	0–2 min
Nitrite derivatization	
Reagent volume (mL)/concrete mass (g)	1.0, 2.0, 3.0, and 4.0
2-AB concentration	0.5, 1.0, 1.8, 3.0, and 3.5%*
H_2SO_4, M	0.05, 0.1, 0.2, 0.3, and 0.4

* Correspond to following 2-AB/nitrite molar ratios: 1.1, 2.1, 4.0, 6.9, and 8.1.

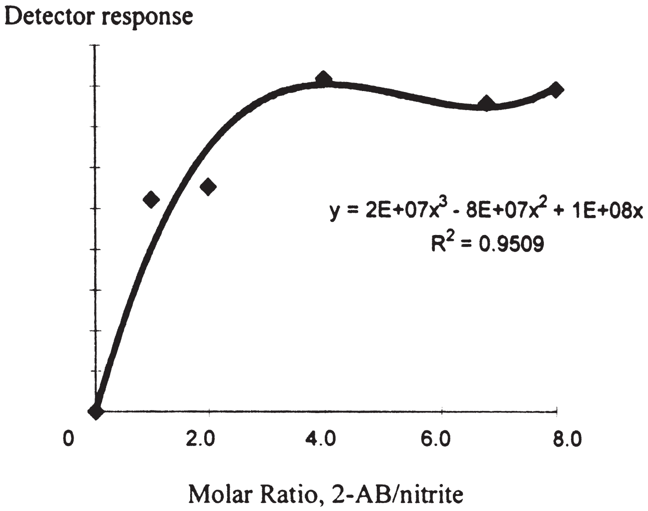

Fig. 2. Detector response for 2-PP as a function of 2-AB/NO_2^- mole ratio. Pyrolysis conditions: 250–850°C at 600°C/min. Concrete sample: 30% $Ca(NO_2)_2$ at 26.7 L/m^3.

maximum at a mole ratio of 4.1 (Fig. 2). The excess 2-AP reagent was probably necesary to satisfy the adsorption by the concrete matrix and provide the driving force to react with the nitrite, some portion of which could exist as the nitrite analog to the monosulfoaluminate hydration product having the approximate formula $[Ca_2Al(OH)_6]NO_2 \cdot nH_2O$ [25].

A wide selection of pyrolysis temperatures was investigated to determine optimum parameters to hydrolyze the 2-phenyl azonium ion to 2-PP, and thermally desorb 2-PP from the concrete matrix. Using a concrete mixture prepared with 4.96 L/m^3 of a 30% $Ca(NO_2)_2$ solution, a programmed temperature run starting at 250°C and ramping up to 850°C with a 1-min hold at 850°C was found to produce the maximum amount of 2-PP (Fig. 3). The ramping capability of the pyroprobe appears to overcome the shortcomings of ballistic heating to specific temperatures. For example, isothermal heating at 250°C is apparently insufficient to thermally desorb the 2-PP derivative, while the relatively low response at 850°C possibly results from decomposition of 2-PP to biphenyl. Interestingly, lowering the programmed heating rate below 600°C/min or extending the hold time beyond 1 min do not appear to increase 2-PP response. The complete set of operating parameters, corresponding to >94% recovery of the originally admixed nitrite for lab-prepared concrete mixtures, is listed in Table 6.

Table 6
Optimum derivatization parameters

Concrete, mass	1 g
Reagent volume	3 mL
Reagent concentration	1% 2-AB in 0.50 M H_2SO_4
Pyrolysis program	250–850°C at 600°C/min with 1-min hold at 850°C

2.1.2. Quantitative analysis

Applying the test parameters listed in Table 6 to the concrete mixtures listed in Tables 1 and 2, the $Ca(NO_2)_2$ recoveries were found to exceed 90% with the exception of one truck mix (Table 7). Included in Table 7 are the recovery values obtained from the earlier referenced wet chemical method with measurement of the extracted nitrite by ion chromatography [7]. For all concrete mixtures, results obtained by Py-GC/MS exceeded those obtained by wet extraction, and are in far better agreement with the originally admixed $Ca(NO_2)_2$ dosages.

The combination of derivatization and thermal desorption appears to more effectively overcome the binding forces between the nitrite and paste fraction of the concrete compared to repetitive aqueous extraction. The cause for the 86

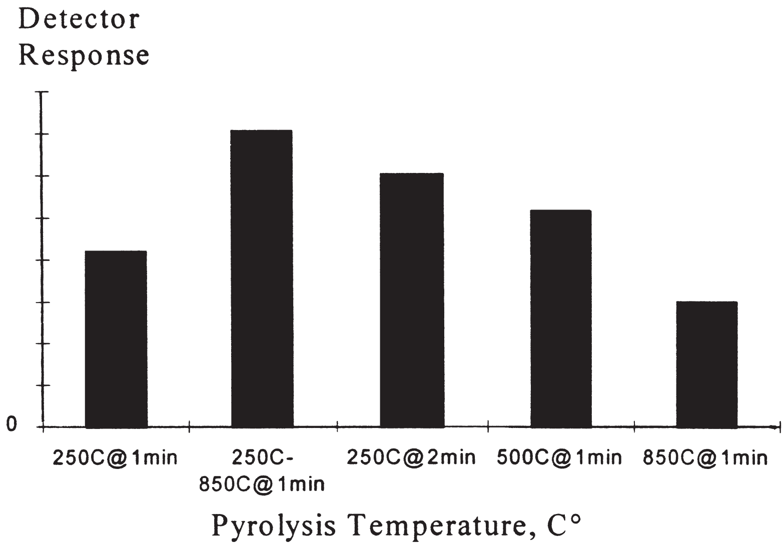

Fig. 3. Detector response for the pyrolytic conversion of 2-AB via nitrosation with nitrite to 2-PP as a function of pyrolysis temperature.

Table 7
$Ca(NO_2)_2$ recovery from concrete

	% Recovery	
	Py-GC/MS	Water extraction/IC
Lab concrete mixtures		
30% $Ca(NO_2)_2$, L/m^3		
4.9	98	72
14.8	94	74
26.7	104	90
Ready-mix concrete		
7.4	112	ND*
12.3	95	77
17.3	86	ND
22.2	90	ND

* ND = not determined.

and 90% recoveries obtained for the 17.3 and 22.2 L/m^3 truck mixes, respectively, is not evident other than the overall truck-to-truck variability for measured $Ca(NO_2)_2$ appears unusually high.

The Py-GC/MS technique offers several attractive features vs. currently used extraction procedures. Duplicate analysis using the water extraction procedure [7] for the four truck-mixed concretes required an intensive 8-h effort, whereas duplicate tests with PY-GC/MS was completed within 2.5 h. 8 L of concrete water extract were generated with the extraction method compared to an essentially solvent-free procedure with PY-GC/MS. Furthermore, unlike the extraction method, the analyst is able to leave the Py-GC/MS instrument unattended other than for sample introduction.

A linear relationship is evident between the detector response for 2-PP vs. $Ca(NO_2)_2$ dosage for both the lab and truck mixed concrete (Table 8). Linearity (and sensitivity) can be improved by operating the MSD in the selected ion-monitoring (SIM) mode, whereby the mass selective detec-

Table 8
Relationship of MSD response as a function of $Ca(NO_2)_2$ dosage

Concrete mix	MSD mode, mass range	Multiple R^2 (coefficient of determination)
Lab	Scan, 45–650 amu	0.975
Lab	SIM, 170 amu	0.996
Truck	SIM. 170 amu	0.982

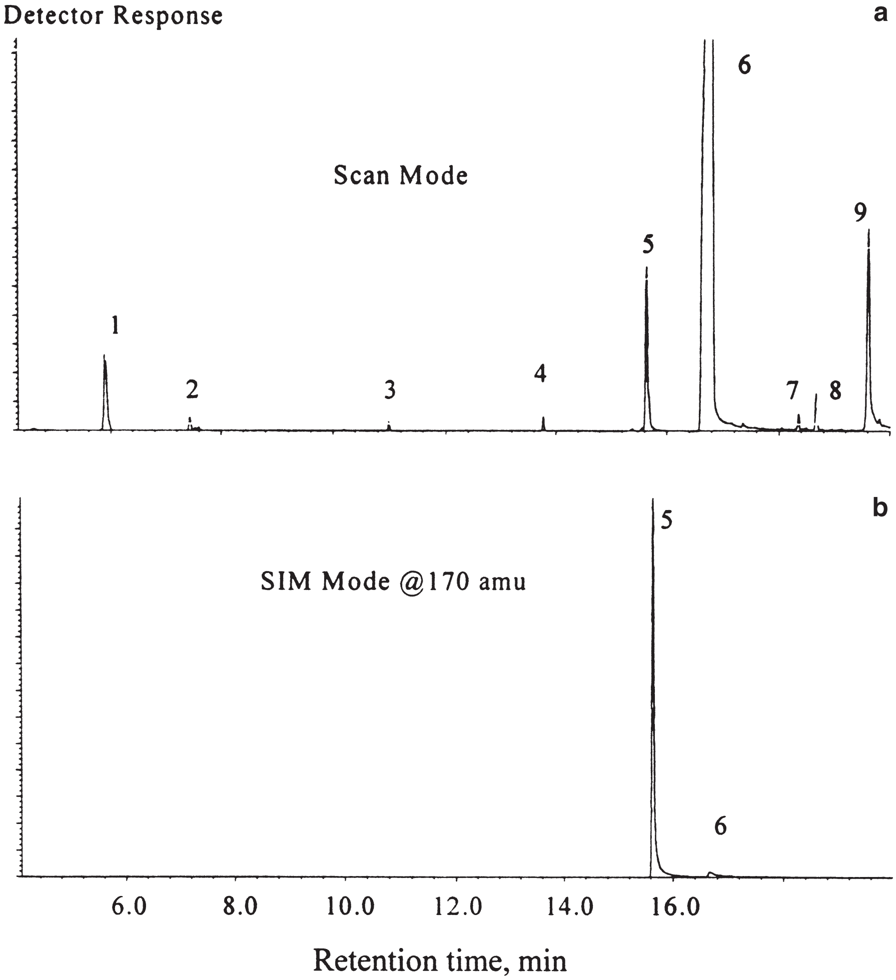

Fig. 4. Scan vs. SIM detection mode for py-GC/MS of $Ca(NO_2)_2$-admixed concrete: *(a)* scan mode; *(b)* SIM mode. Peak identification: 1 = styrene, 2 = 1-methylstyrene, 3 = benzothiophene, 4 = biphenyl, 5 = 2-PP, 6 = 2-AB, 7 = unknown, 8 = dibenzothiophene, 9 = 9H-carbazole.

tor is set to monitor only those compounds whose mass spectrum features a particular molecular mass or ion clusters. The SIM mode greatly minimizes background noise and interference from closely eluting compounds. A comparison of the MSD output for the scan (45–650 amu) vs. SIM (170 amu) modes, obtained from the Py-GC/MS analysis of a concrete mixture admixed with 14.8 L of 30% $Ca(NO_2)_2/m^3$, illustrates the improved selectivity for the 2-PP derivative (Fig. 4). The standard deviation was determined by pyrolyzing 12 different concrete samples in duplicate. The resulting pooled standard deviation was 0.8 L/m^3, with a relative standard deviation (RSD) of 5%.

The presence of various common admixtures were not found to significantly interfere with the Py-GC/MS method for nitrite in concrete (Table 9).

Chemical analysis for nitrite content is often included as part of the ongoing condition assessment of steel-reinforced concrete structures admixed with calcium nitrite corrosion inhibitor to help predict future durability [26]. The Py-GC/MS and wet chemical methods were applied for the analysis of 50-mm diameter cores removed from two bridge decks constructed in 1986 (Table 10).

Results from the Py-GC/MS and wet chemical methods are generally comparable, and indicate that all of the originally admixed $Ca(NO_2)_2$ appears to be present in the bridge deck after 14 years of service. The cause for the measured $Ca(NO_2)_2$ dosages being higher than the specified 19.7 L/m^3 addition rate, especially for bridge GPB, may possibly be due to sampling bias as the single 50-mm diameter cores submitted for analysis could have been deficient in coarse aggregate.

2.2. SRA determination

Since the glycol-ether blend has been commercially available for just over 1 year, prior methods have not been reported because of the limited need to estimate this admixture in concrete. The feasibility of using thermal desorption coupled with GC/MS was evaluated using a series of mortar mixes described in Table 3.

Attempts to extract the glycol-ether blend from pulverized (-300 μm) portions of mortar using 2-propanol with sonication resulted in very low recovery rates ($<18\%$), suggesting possible chemisorption with the hydrating cement phases. TD-GC/MS was regarded as an attractive method for SRA determination in concrete because the SRA composition consists of volatile compounds. A comparison of the total ion chromatograms (TIC) obtained from injecting a solution of SRA and the TIC produced from heating a mortar mixture admixed with SRA (Fig. 5) confirms that simple desorption from the mortar matrix occurs as opposed to thermal degradation to other volatile compounds.

Table 9
Effect of common admixtures on Py-GC/MS of concrete for $Ca(NO_2)_2$ content*

Admixture	Dosage (L/m^3)	% Recovery
Control	—	98
Lignin/TEA	0.6	105
NSFC/lignin	2.4	104
Lignin/corn syrup	0.6	101
Lignin/TEA/corn syrup	0.6	93

* Added as a 30% solution.

Table 10
30% $Ca(NO_2)_2$ (l/m^3) in field structures*

		Determined dosage	
Bridge code	Specified dosage	Py-GC/MS	Wet chemical
WBP	19.7	21.2	21.7
GPB	19.7	31.0	28.1

* 95% confidence limits for the average from duplicate runs are ± 1.61 L/m3.

Since the concentration of the glycol-ether blend in the mortar mixtures could exceed the normal operating range of the MSD system, all the mortars were diluted tenfold by intergrinding a 2-g portion with 18 g of control mortar as described earlier for the nitrite procedure. Using 70 mg of the 5200 ppm mortar mixture, a wide range of ballistic and ramped heating programs were evaluated to determine thermal desorption parameters for optimum recovery. The mortar sample was allowed to cure for 7 days at 100% relative humidity prior to crushing. Recovery rates were based on comparing the sum of area responses from seven peaks corresponding to the glycol-ether blend, obtained by introducing 2 μL of a 2.5% SRA solution in acetonitrile on 70 mg of control mortar, to the area response produced by thermal desorption of the admixed mortar. The results summarized in Table 11 indicate that maximum recovery occurs with ballistic heating at 700°C.

The relatively low recovery obtained with temperature ramping could possibly result from the formation of nonvolatile complexes between the glycol ether blend and various hydrating cement phases that would not be detected by GC-MS. Similarly, ballistic heating at 900°C appears to cause loss of the SRA compounds probably due to thermal degradation.

A linearity study of the TD-GC/MS method, performed with five mortar samples that were diluted tenfold with a control mortar, found the multiple R^2 (coefficient of determination) to be 0.998. The concentrations of SRA in the mortar samples after dilution were 0, 130, 260, 520, and 780 ppm. Thermal desorption on the 5200-ppm mortar, prepared with four other commercial cements, #051, #143, #170, and #017 along with a mortar admixed with both SRA and an NSFC-based superplasticizer, suggest that both cement composition and NSFC admixtures have a minimal effect on effect on the recovery rate of the SRA (Table 12). TD-GC/MS analysis of mortar (or concrete) mixtures, prepared with a wider range of cements and cement-pozzolan blends, are required to better understand effect of binder composition on SRA measurement.

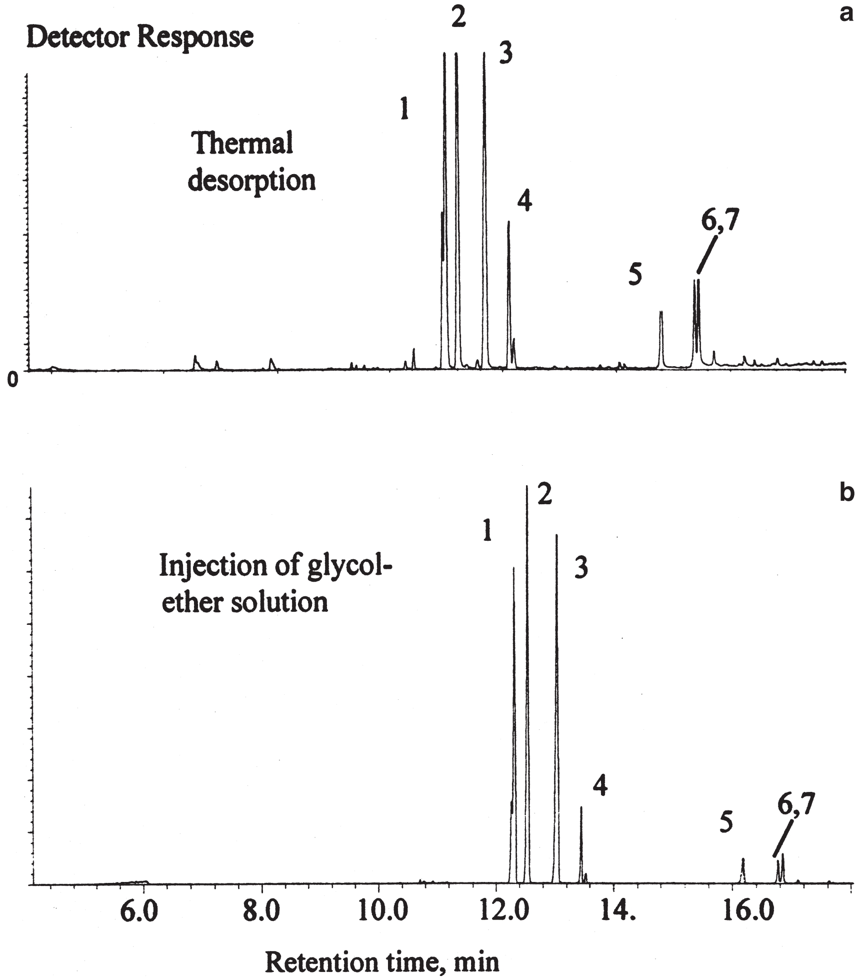

Fig. 5. TD-GC/MS of mortar admixed with 780 ppm SRA. Peaks 1 through 7 are associated with the glycol-ether blend.

The pooled standard deviation for 12 pairs of replicate measurements of the thermally desorbed glycol-ether blend from mortar was 130 ppm, which corresponds to an RSD of 4%.

3. Conclusion

The described thermal GC/MS methods can greatly facilitate the determination of certain durability-enhancing chemical admixtures in hardened concrete. In the case of a nitrite-based corrosion inhibitor, the role of nitrite (as nitrous acid) for the conversion of 2-AB to 2-PP and subsequent detection by GC-MS, has found nitrite measurement to be both quantitative and selective. Direct thermal desorption of the glycol-ether blend from various mortar samples also indicates that quantitative estimates of SRA content in cementitious mixtures are feasible. The benefits provided by thermal GC/MS methods include significant time savings vs. wet chemical extractions, near elimination of sol-

Table 11
% Recovery of SRA from mortar as a function of heating parameters

Heating process	SRA, % recovery*
Ballistic	
300°C at 1 min	63
500°C at 1 min	85
700°C at 1 min	93
900°C at 1 min	78
Ramped	
200–800°C, 600°C/min	60
200–800°C, 600°C/min, with 1 min hold at 800°C	57

* 95% confidence limits based on the average of duplicate runs are ±6%.

Table 12
Effect of cement brand and NSFC superplasticizer on SRA recovery

Cement used in mortar	% SRA recovery from mortar*
#133	94
#051	99
#143	87
#170	91
#017	87
#133, NSFC	95

* 95% confidence limits based on the average of duplicate runs are ±6%.

vent handling, and more consistent measurement of the original admixture content. Considering that the range of cementitious compositions in this study was limited, further work needs to be done to understand the effect of additional cements, pozzolans, chemical admixtures, and age of the concrete on the recovery of both the $Ca(NO_2)_2$-based corrosion inhibitor and glycol-ether SRA blend.

Acknowledgments

The authors wish to thank Boris Gitlin for his assistance in performing the thermal GC-MS analyses, and W.R. Grace for permission to publish this work.

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