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Determination of Four Quinones in Diesel Exhaust Particles, SRM 1649a, and Atmospheric $PM_{2.5}$

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Quinones are reactive organic compounds and are known to initiate reactions associated with many toxicological events. Their presence in air pollution has been demonstrated, but routine quantitative measurements are lacking. A quantitative method for the determination of four quinones was developed using diesel exhaust particles (DEP) and National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1649a. The method was then used to analyze ambient air samples from different sites in Southern California. After extraction in dichloromethane, the target compounds were converted to their stable diacetyl derivatives and determined by electron impact GC-MS using selected ion monitoring. Calibration plots were obtained with deuterium-labeled internal standards. The four quinones, 1,2-naphthoquinone (1,2-NQ), 1,4-naphthoquinone (1,4-NQ), 9,10-phenanthraquinone (9,10-PQ), and 9,10-anthraquinone (9,10-AQ), were quantified in DEP, in SRM 1649a, and in ambient air samples of $PM_{2.5}$ collected in several rural and urban sampling locations upwind and downwind of major emission sources in Central Los Angeles. Mean concentration of individual target quinones ranged from 7.9–40.4 μg/g in the DEP, and from 5–730 pg/m^3 in the $PM_{2.5}$ samples. Precision (repeatability and reproducibility) varied from 2–22%. Further measurements of these species in future air samples should be considered in light of their potential health significance.

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INTRODUCTION

Quinones are toxicologically important components of air pollution. They have been found in ambient particulate matter (Allen et al. 1997; Fraser et al. 1998; Simoneit et al. 1991), automotive exhaust emissions (Schuetzle et al. 1981), and wood smoke particles (Fine et al. 2001; Ramdahl 1985). Quinones and their reduction products, semiquinones and hydroquinones, are of toxicological interest because of their ability to generate reactive oxygen species and to form covalent bonds with tissue macromolecules (Cadenas et al. 1992; Monks and Lau 1992;

Henry and Wallace 1996). The toxicology of naphthalene and phenanthrene quinones has been well-documented (Flowers-Geary et al. 1996; Henry and Wallace 1996; Bolton et al. 2000).

We report here a method developed for the quantification of the four quinones, 1,2-naphthoquinone (1,2-NQ), 1,4-naphthoquinone (1,4-NQ), 9,10-phenanthraquinone (9,10-PQ), and 9,10-anthraquinone (9,10-AQ), that are present in diesel exhaust particles (DEPs) and National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1649a at μg/g levels, and in ambient $PM_{2.5}$ samples collected from sites located in Central California and in the Los Angeles Basin (LAB) at pg/m^3 levels. These compounds are of interest because of their toxicity (Flowers-Geary et al. 1996; Henry and Wallace 1996; Penning et al. 1996; Bolton et al. 2000) and their presence, or the presence of their precursors (Schuetzle et al. 1981; Finlayson-Pitts and Pitts 2000), in ambient air. The assay developed was GC-MS based, using deuterated internal standards and selected ion monitoring (SIM). The target compounds were converted to their diacetyl derivatives with a mixture of zinc and acetic anhydride, and were subsequently analyzed by GC-MS.

MATERIALS AND METHODS

Chemicals

Acetic anhydride (Fisher, Tustin, CA, USA) and the solvents acetonitrile and dichloromethane (EM Science, Gibbstown, NJ, USA), hexane (Fisher, Tustin, CA, USA), pentane (EM Science, Gibbstown, NJ, USA), and tetrahydrofuran (Aldrich, Milwaukee, WI, USA) were obtained from the indicated sources and were reagent-grade or the highest grade available. The quinones (d0) were obtained from Aldrich Chemical Co. (Milwaukee, WI, USA) and the zinc from Fisher (Tustin, CA, USA). Deuterium-labeled hydrocarbons used to synthesize the internal standards were obtained from Cambridge Isotope Laboratories (anthracene-d10, phenanthrene-d10), Isotec Inc. (1-naphthol-d7), and Aldrich Chemical Co. (naphthalene-d8).

Deuterium-Labeled Internal Standards

Deuterium-labeled internal standards were prepared from the hydrocarbon precursors using published synthetic procedures for the target quinones. Thus, 1,2-napthoquinone-d6 used the procedure of Krohn et al. (1990), 1,4-naphthoquinone-d6 that of Braude and Fawcett (1953), 9,10-anthraquinone-d8 that of Underwood and Walsh (1943), and 9,10-phenanthraquinone-d8 the procedure of Oyster and Adkins (1921). The identity and purity of the synthetic compounds were based on NMR, TLC, and mass spectra analyses. All standards were stored at -80°C in vials containing sufficient quantities for a single standard curve, so that each stored sample was opened only once.

Sample Sources

Diesel Exhaust Particles. Details of sampling conditions for these particles are described elsewhere (Sagai et al. 1993). In brief, they were generated by a light-duty (2740 cc) four-cylinder diesel engine (4BJ type, Isuzu Automobile Co., Tokyo, Japan) using standard diesel fuel. The engine was operated at 2000 rpm under 6 torque (kg/m) generated by an EDYC dynamometer (Meidensya, Tokyo, Japan). DEPs accumulated for three months in the dilution tunnel were collected on glass fiber filters (203 mm $\times$ 254 mm) in a constant-volume sampler system attached to the end of the dilution tunnel.

Standard Reference Material 1649a. This SRM material, collected in Washington DC, is the first particle-based environmental natural matrix. It is the most extensively characterized natural matrix available from NIST. It was primarily intended for use in the evaluation and calibration of analytical methods for the determination of trace-level organic constituents present in atmospheric particulate matter (Wise et al. 2000).

Ambient Air $PM_{2.5}$ Samples. Seventeen samples were collected for continuous sampling periods of 24 h in three California communities: Atascadero (a rural location some 350 km northwest of Los Angeles), San Dimas (a mid-basin location approximately 50 km downwind of metropolitan Los Angeles), and Riverside (in the urban plume some 90 km downwind of Los Angeles). Ambient air sampling sites were established atop one-story school district buildings in Atascadero and San Dimas. In Riverside, a sampling location was established in the middle of a several-hundred acre agricultural research area on University of California (Riverside) property. Samples were collected using a commercially available sampler (Tisch Environmental Inc. model 1202 Sampler) operated at a mass flowmeter-controlled sampling rate of 113 L/min with a $PM_{2.5}$ inlet particle size cut-point. Filters were loaded into field sampling units within 12 h of sample initiation, sampled using automated timer programming, and retrieved within 12 h of sampling completion. $PM_{2.5}$ samples were collected on 100 mm diameter quartz fiber filters (Whatman number 1851-101), prebaked for 16 h at 550°C. After sampling, the filters were placed in refrigerated portable ice chests and returned to the laboratory, where they were kept in a freezer before analysis.

DEP and SRM 1649a Extraction. Dichloromethane (DCM, 5 mL) and internal standards were added to test tubes containing ca. 1–2 mg (weighed to $\pm$0.02 mg) of DEP (Sagai et al. 1993) or SRM 1649a. The tubes were capped and ultrasonicated for 30 min, then centrifuged for 10 min at 2000 rpm. The clear supernatants were then subjected to the analytical protocol described below. The efficiency of the DCM extraction for the DEP quinones was assessed by a second extraction of the residue from the first. The quinone in the second extract represented less than 5% of the first extract, so all subsequent analyses were performed on samples from a single extraction.

Extraction of $PM_{2.5}$ Samples. The quartz fiber filters were placed in 20 mL amber vials with Teflon-lined caps and extracted by ultrasonication with 15 mL of DCM during three periods of 8 min each, replacing the bath water between periods to avoid overheating. The resulting suspension was filtered using a 5.0 μm nylon membrane filter. The extract was placed inside an empty desiccator to reduce the sample volume to $\sim$5 mL by evaporation.

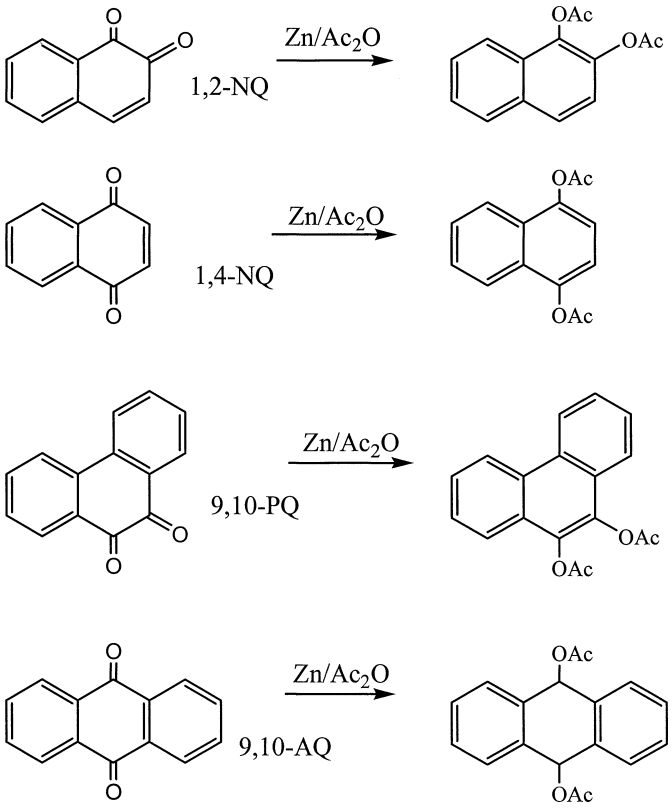

Figure 1. The quinones and their derivatizations.

Chemical Analysis

Following sample extraction, the quinones were converted to their diacetyl derivatives, as shown in Figure 1. In the procedure, approximately 3/4 of the final extract aliquot volume was transferred to conical tubes and evaporated under nitrogen to ca. 50 μL. A portion of zinc ($\sim$100 mg) and 200 μL acetic anhydride was then added. The capped tubes were mixed well and heated on an 80°C heating block for 15 min, mixing on a vortex every 5 min. The samples were cooled to room temperature, and an additional similar portion of zinc was added. The tubes were capped again and heated for an additional 15 min with 5 min mixing intervals. The reaction was quenched by addition of 0.5 mL water and 3.0 mL of pentane. The samples were mixed and centrifuged at 2000 rpm for 10 min. The pentane layer was concentrated by evaporation to dryness and the sample reconstituted in 80 μL dry acetonitrile and 1 μL was injected into the GC-MS system.

The GC-MS system consisted of an Agilent (HP) 6890 Plus GC System equipped with a 6890 series injector and interfaced to a 5973 Mass Selective Detector (MSD). An HP-5MS capillary column (0.25 mm id, 0.25 μM film thickness, 30 m) was used to separate the acetylated derivatives. Initial column temperature was maintained at 100°C for 4.0 min then ramped to 280°C at a rate of 5°C/min. Column flow was 1.0 ml/min. Retention times and monitored ions are shown in Table 1.

Calibration plots were obtained for standards of 1,2-NQ, 1,4-NQ, 9,10-PQ, and 9,10-AQ, and the internal standards, 1,2- and 1,4-NQ-d6, 9,10-PQ-d8, and 9,10-AQ-d8. For this purpose, the quinones and internal standards were dissolved in dry tetrahydrofuran (total volume 0.3 mL) and carried through the acetylation procedure. Standard addition experiments were used to determine recoveries from the DEP samples. The recoveries found for triplicate analyses $\pm$ s.d. were 105 $\pm$ 5% (1,2-NQ), 132 $\pm$ 30% (1,4-NQ), 108 $\pm$ 5% (9,10-PQ), and 104 $\pm$ 3% (9,10-AQ). Recoveries for the SRM 1649a samples were somewhat lower, ranging from 55% (1,4-NQ) to 90% (9,10-AQ). The differences in recoveries observed for DEP and SRM 1649 may reflect the varying chemical nature of the matrix.

RESULTS AND DISCUSSION

The two-fold objectives of this research were based on the important toxicological properties of quinones, which may have a role in the health effects associated with exposure to ambient particulate matter, and associated vapor phase copollutants. The first objective was the development of a GC-MS method for the quantitative estimation of quinones, and the second objective was to apply the methodology to determine the presence of four quinones in ambient air samples from different regions of the Los Angeles basin for illustrative purposes.

Table 1
Selected ion monitoring conditions

Quinone	Retention time min	Monitored ions m/z, (mass fragments)
1,2-Naphthoquinone (1,2-NQ)	25.30	160.1* (M-2CH_2CO^+), 202.0 (M-CH_2CO^+), 244.0 (M^+)
1,4-Naphthoquinone (1,4-NQ)	26.52	160.1* (M-2CH_2CO^+), 202.0 (M-CH_2CO^+), 244.0 (M^+)
9,10-Phenanthraquinone (9,10-PQ)	36.11	210.1* (M-2CH_2CO^+), 252.0 (M-CH_2CO^+), 294.0 (M^+)
9,10-Anthraquinone (9,10-AQ)	36.45	210.1* (M-2CH_2CO^+), 252.0 (M-CH_2CO^+), 294.0 (M^+)
1,2-Naphthoquinone-d6 (1,2-NQ-d6)	25.25	166.1* (M-2CH_2CO^+)
1,4-Naphthoquinone-d6 (1,4-NQ-d6)	26.47	166.1* (M-2CH_2CO^+)
9,10-Phenanthraquinone-d8 (9,10-PQ-d8)	36.04	218.1* (M-2CH_2CO^+)
9,10-Anthraquinone-d8 (9,10-AQ-d8)	36.38	218.1* (M-2CH_2CO^+)

*m/z used for quantitation.

(a) Underivatized 1,2-naphthoquinone-d0 & 1,4-naphthoquinone-d0

1,2-diacetoxynaphthalene-d0 & 1,4-diacetoxynaphthalene-d0

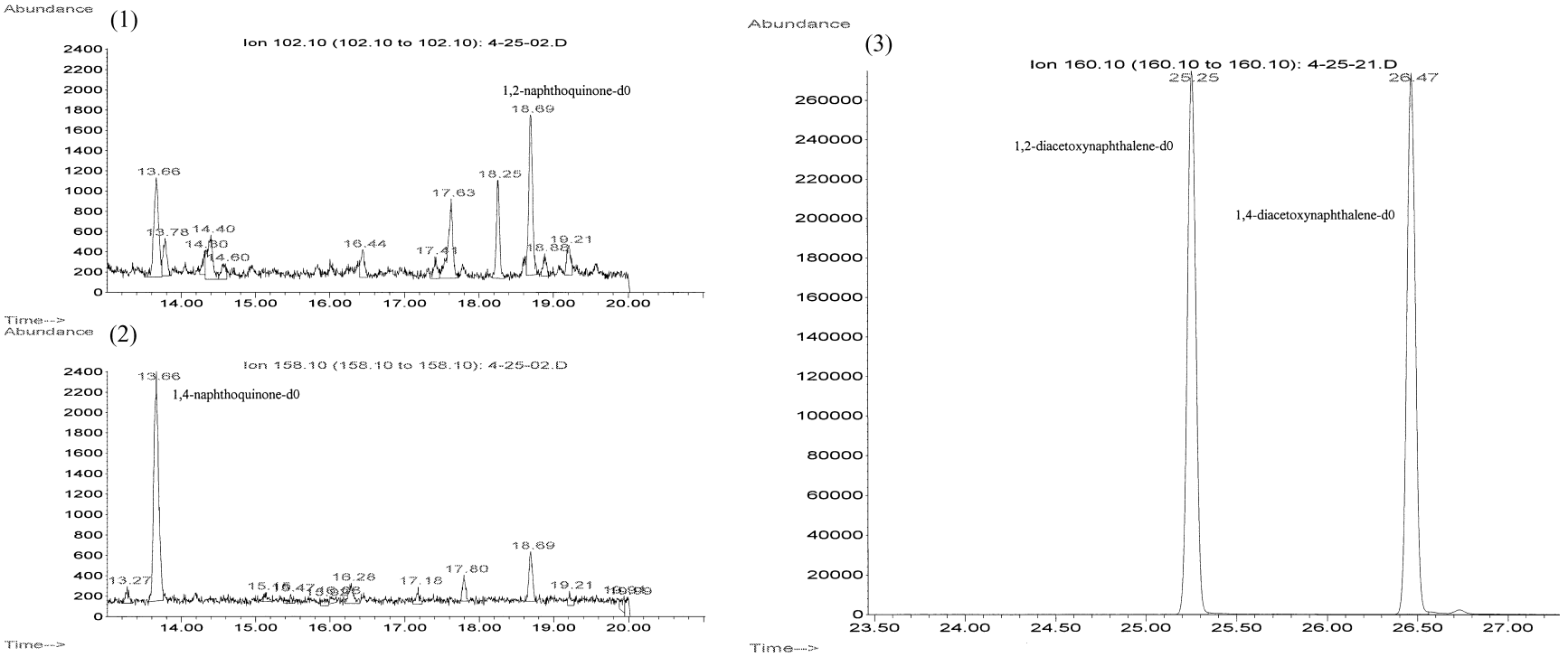

Figure 2. (a) SIM tracings of underivatized 1,2-naphthoquinone-d0 and 1,4-naphthoquinone-d0 (left panel) versus their acetylated derivatives (right panel). Quantities of 3.3 ng of each compound were injected. (1) Ion 102.10 was used to monitor underivatized 1,2-naphthoquinone-d0. (2) Ion 158.10 was used to monitor 1,4-naphthoquinone-d0. (3) Ion 160.10 was used to monitor acetylated 1,2 and 1,4-naphthoquinone-d0. Note the differences in the abundance scale. (b) SIM tracings of underivatized 9,10-phenanthraquinone-d0 and 9,10-anthraquinone-d0 (left panel) versus their acetylated derivatives (right panel). Quantities of 3.3 ng of each compound were injected. (1) Ion 180.10 was used to monitor underivatized 9,10-phenanthraquinone-d0. (2) Ion 208.10 was used to monitor 9,10-anthraquinone-d0. (3) Ion 210.10 was used to monitor acetylated 9,10-phenanthraquinone-d0 and 9,10-anthraquinone-d0. Note the differences in the abundance scale. *(Continued)*

(b) Underivatized 9,10-phenanthraquinone-d0 & 9,10-anthraquinone-d0

9,10-diacetoxyphenanthrane-d0 & 9,10-diacetoxyanthracene-d0

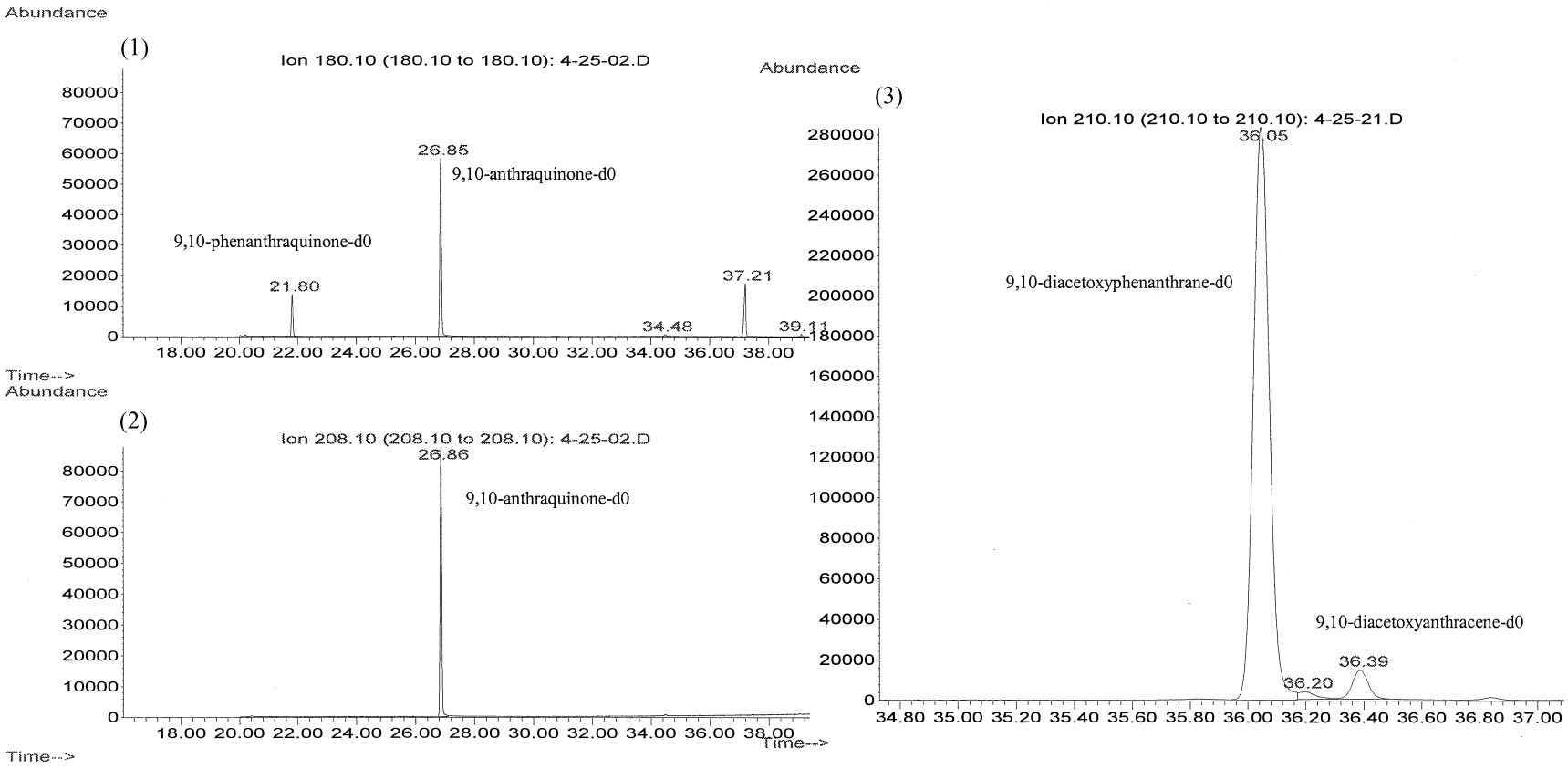

Figure 2. (Continued)

Table 2
Comparison of the limits of detection of the derivatized and underivatized quinones

Quinone	LOD (ng) Underivatized	Derivatized	Ratio
1,2-Naphthoquinone (1,2-NQ)	29.0	0.3	95.9
1,4-Naphthoquinone (1,4-NQ)	16.3	0.4	38.0
9,10-Phenanthraquinone (9,10-PQ)	3.8	0.2	15.6
9,10-Anthraquinone (9,10-AQ)	1.5	4.8	0.3

Standard curve samples of the indicated quinones were prepared as described in METHODS. The limits of detection values represent the analyte values when the peak height to noise ratio is three.

The optimal conditions for extraction, reduction, derivatization, and chromatography were established with standards and extracts from DEP. The availability of a large sample of DEP allowed us to develop the analytical procedure and perform multiple determinations to evaluate the reproducibility of the method. In preliminary experiments, attempts to develop the assay with underivatized naphthoquinones were not successful because of their instability in solution and their lower sensitivity in a GC-MS assay (Figure 2a). Table 2 compares the limits of detection (LOD) for the underivatized and derivatized assays. With the exception of 9,10-AQ, the limits of detection were higher for the underivatized procedure (Figure 2b). The difference in sensitivity between the derivatized and underivatized quinones can be seen by comparing the abundance of each peak, since equal amounts were injected in all tracings. Figure 3 shows typical calibration curves (2.5–250 ng) for the 4 acetylated quinones. The %CV for the slopes between days was $<12\%$ ($n = 4$). When hydroquinone standards were processed through the present procedure, less than 10% of their amounts could be detected, so that as proposed, the assay appears to be selective for quinones. Results of application of the finalized procedure to the DEP are shown in Table 3. All four quinones were found in quantifiable

Table 3
Quinone concentrations (μg/g) in DEP

Compound	MW	*N*	Mean[a]	*SD*	RSD%
1,2-NQ	158.16	4	13.69	2.97	22
1,4-NQ	158.16	4	7.93	0.81	10
9,10-PQ	208.22	4	24.19	2.11	8
9,10-AQ	208.22	4	40.41	0.96	2

[a]The values represent the mean obtained from four separate weightings, each determined with a single injection.

Table 4
Quinone concentrations (μg/g) in SRM 1649a

	Number of samples	Mean*	*SD*	RSD%
1,2-NQ	12	0.19	0.026	14
1,4-NQ	12	0.24	0.054	23
9,10-PQ	12	1.18	0.130	11
9,10-AQ	12	2.03	0.192	9.0

*The values represent the mean of 12 separate weightings, each determined with a single injection.

levels in this sample. The variability between analyses ranged from 2–22%, with 1,2-NQ being the highest. In DEP, levels of the three-ring quinones, 9,10-PQ and 9,10-AQ, were higher than those for the more volatile 2-ring compounds.

SRM 1649a. The target quinones were also found and measured in the urban dust SRM 1649a. The mean concentrations ranged from 0.19 μg/g for 1,2-NQ to 2.03 μg/g for 9,10-AQ, with % RSDs varying from 9–23% (Table 4). Durant et al. (1998) have reported a value of 2.7 ± 0.12 μg/g for 9,10-anthraquinone in this SRM. The levels of 9,10-AQ are comparable to those found by these investigators, but they do not report values for 1,2-NQ, 1,4-NQ, and 9,10-PQ. To our knowledge, this is the first quantitative report of 1,2-NQ, 1,4-NQ, and 9,10-PQ in SRM 1649a.

Atmospheric $PM_{2.5}$. The assay developed was applied to ambient air samples collected at several locations in Southern California. The results are summarized in Table 5. Quinone concentrations in the airborne $PM_{2.5}$ were determined from samples collected in Atascadero, San Dimas, and Riverside. One striking observation is that 9,10-AQ (at levels of 20–200 pg/m^3) was ubiquitous at the three study sites. In the more rural agricultural area of Atascadero, although levels of 1,2-NQ, 1,4-NQ,

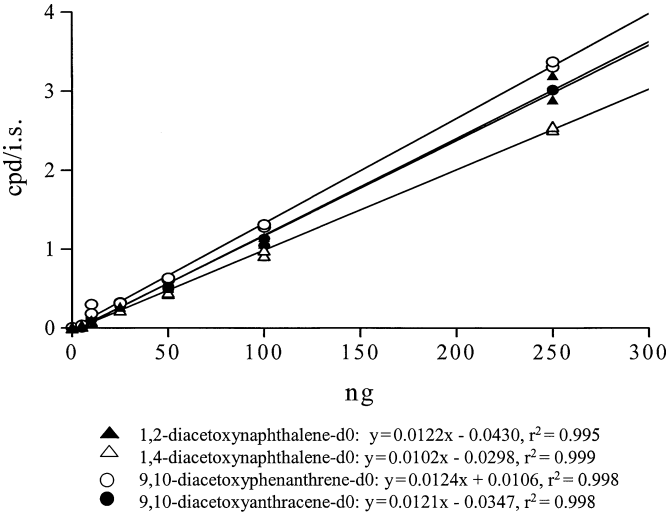

Figure 3. Representative calibration curves for the four quinones.

Table 5
Quinone concentrations (pg/m^3) in the airborne $PM_{2.5}$

Atascadero /date		6/7/01	6/15/01	6/21/01	6/27/01	6/15/01
1,2-NQ		<LOD	<LOD	<LOD	<LOD	<LOD
1,4-NQ		5.0	17	10	6.0	<LOD
9,10-PQ		<LOD	18	6.0	11	<LOD
9,10-AQ		100	120	130	160	200
San Dimas	5/31/01	6/7/01	6/13/01	6/19/01	6/25/01	7/13/01
1,2-NQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
1,4-NQ	110	110	100	140	130	60
9,10-PQ	330	430	150	330	370	<LOD
9,10-AQ	150	100	130	170	180	50
Riverside	5/31/01	6/7/01	6/13/01	6/19/01	6/25/01	7/13/01
1,2-NQ	<LOD	40	<LOD	<LOD	<LOD	60
1,4-NQ	<LOD	170	60	130	90	230
9,10-PQ	<LOD	480	130	730	270	570
9,10-AQ	20	60	80	170	160	200

Values are based on single injections.

and 9,10-PQ were comparatively much lower (5–18 pg/m^3), observed levels of 9,10-AQ were remarkably similar to the levels found in urban San Dimas (in the Los Angeles metropolitan area), and further downwind in Riverside. Although similar levels of 9,10-AQ have been reported for Los Angeles sites by Fraser et al. (1998), and much higher levels for Porte D'Auteuil, France (Leotz-Gartziandia et al. 2000), we are currently investigating the possibility that some of the 9,10-AQ found in our $PM_{2.5}$ samples may have resulted from its formation on the filter surface during sample collection. In San Dimas and Riverside, the profiles of 1,4-NQ and 9,10-PQ were similar, suggesting a common or regional source for these quinones. Likely sources for these compounds would include direct vehicle emissions and formation during regional atmospheric transport. Levels of 9,10-PQ were considerably higher in samples collected in San Dimas and in Riverside compared to rural Atascadero, where automotive exhaust emissions are much lower.

Levels of naphthoquinones on the quartz filters were lower than those of 9,10-PQ and 9,10-AQ. This is somewhat inconsistent when compared to the levels of the corresponding hydrocarbons, since they are likely to be oxidation products from either combustion or atmospheric reactions. Historically, naphthalene has been found in atmospheric samples at 50 to 275 times higher levels than phenanthrene (Finlayson-Pitts and Pitts 2000). One possible explanation for this apparent inconsistency may be that most of the naphthoquinones are present in the vapor-phase. In preliminary experiments examining vapor-phase quinones present in ambient air, trapped below the quartz fiber filter (QF) by an XAD-4 resin bed (XAD), we have found extremely high levels of both 1,2- (53–440 pg/m^3) and 1,4-NQ (577–9710 pg/m^3). Figures 4a and b show total ion chromatogram (TIC) tracings of an ambient extract from Lake Arrowhead (QF & XAD). The retention times and monitored mass ratios (Figures 5a and b) were compared with standards (Figures 6a and b) and confirmed the identity of the quinones in the samples.

The level of 9,10-PQ (427 pg/m^3) found in particulate matter samples collected in Boston (Allen et al. 1997), and of 9,10-AQ found in Los Angeles (mean of 360 pg/m^3) in samples collected in 1993 (Fraser et al. 1998) were similar to the 9,10-PQ levels (130–730 pg/m^3) found in this study in San Dimas and Atascadero. The presence of 9,10-PQ and the naphthoquinones in ambient air samples has important toxicological implications. Kumagai and his associates reported previously that 9,10-PQ is a potent inhibitor of neuronal form of nitric oxide synthase (NOS) (Kumagai et al. 1998). They have recently shown that 9,10-PQ also inhibits the endothelial form of NOS, which plays a critical role in vascular tone, thereby causing the suppression of NO-dependent vasorelaxation of aorta and significant increase in blood pressure in rats (Kumagai et al. 2001). The mechanisms involved in these actions generalize to other quinones (Kumagai et al. 1998) so that the presence of multiple quinones in particulate matter could contribute to a greater effect than that from 9,10-PQ alone. These observations could be relevant to epidemiological studies, which have suggested an association of ambient particulate matter such as $PM_{2.5}$ with cardiopulmonary diseases and mortality (Dockery et al. 1993; Pope et al. 1995, 2002 ACS study reference; Borja-Aburto et al. 1998).

CONCLUSIONS

This method was applied to ambient $PM_{2.5}$ collected in one rural and two urban sites in Southern California. The results show that the present method allows the quantification of quinones, including the previously unreported 1,2-NQ in ambient air particulate samples at the pg/m^3 range. Sampling sites

(a)

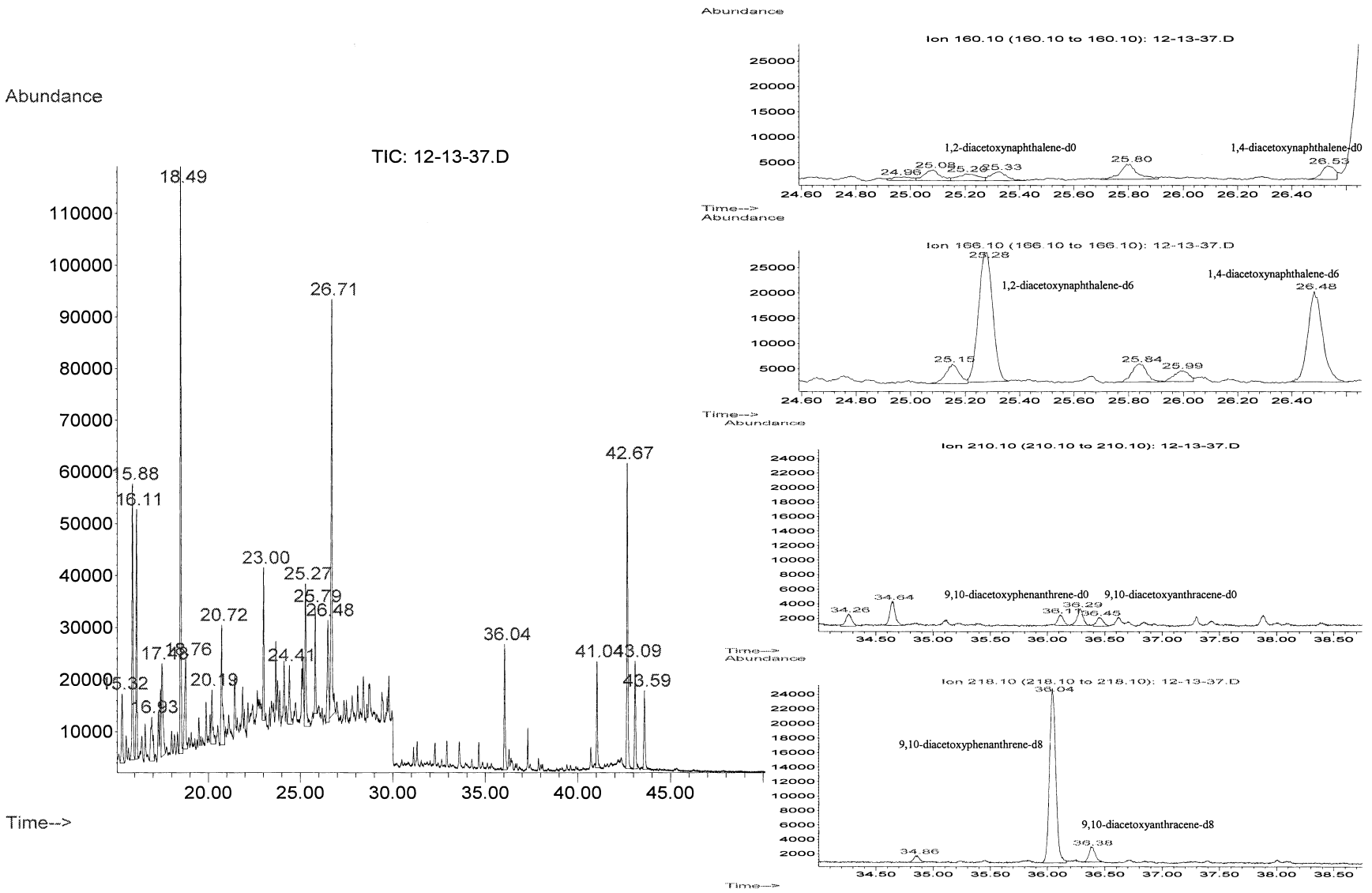

Figure 4. (a) TIC & SIM tracing of an actual ambient sample trapped above the quartz fiber filter (QF) from Lake Arrowhead, CA on 23 September 2002. Deuterated internal standards are used to identify the peaks with respect to retention time shift due to matrix. The SIM tracings are shown on the right of the TIC tracing. (b) TIC & SIM tracing of an actual ambient sample trapped by a XAD-4 resin bed from Lake Arrowhead, CA on 23 September. Deuterated internal standards are used to identify the peaks with respect to retention time shift due to matrix. The SIM tracings are shown on the right of the TIC tracing. *(Continued)*

(b)

LAH020923-XAD TIC & SIM
(Acetylated)

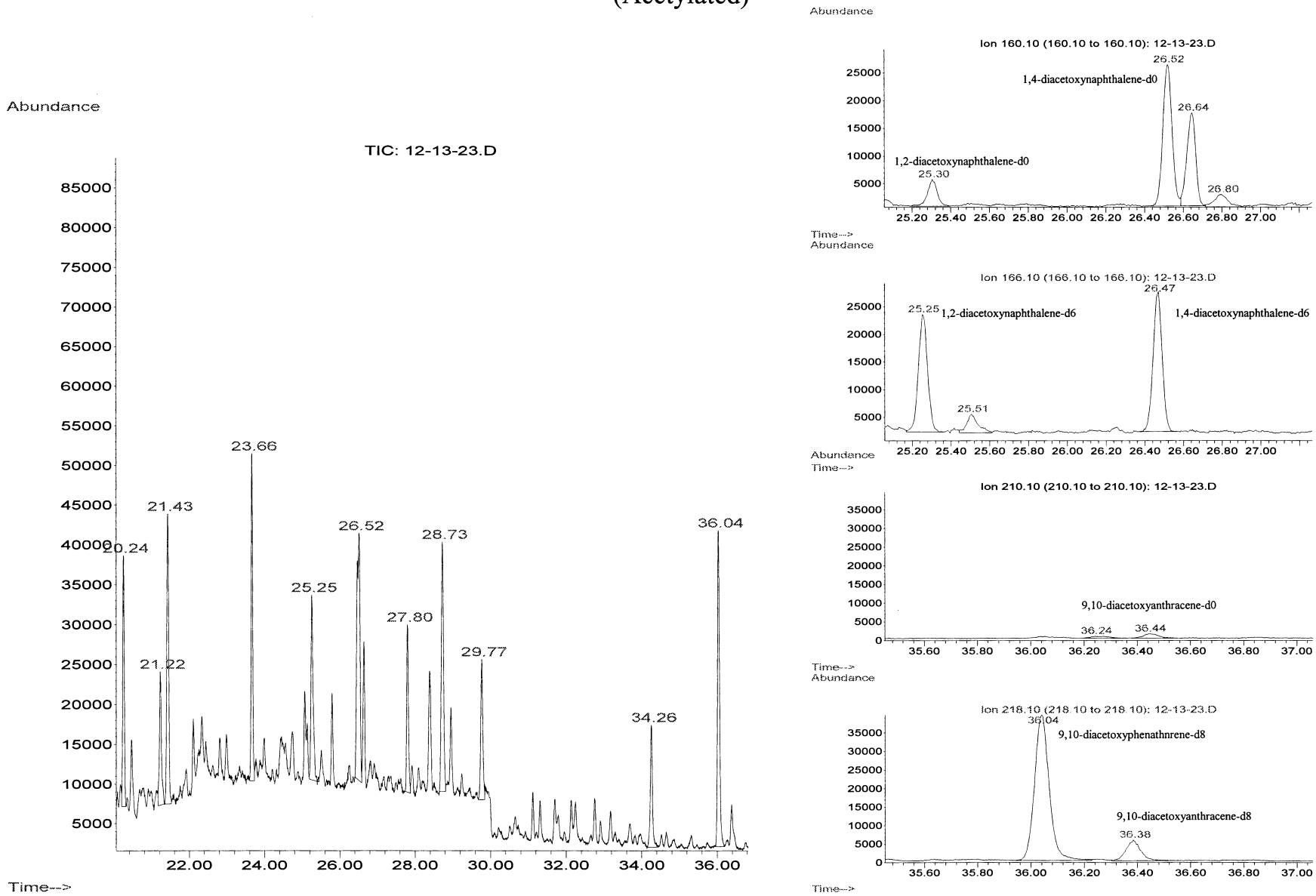

Figure 4. (Continued)

(a) LAH020923-XAD (SIM & SCAN)

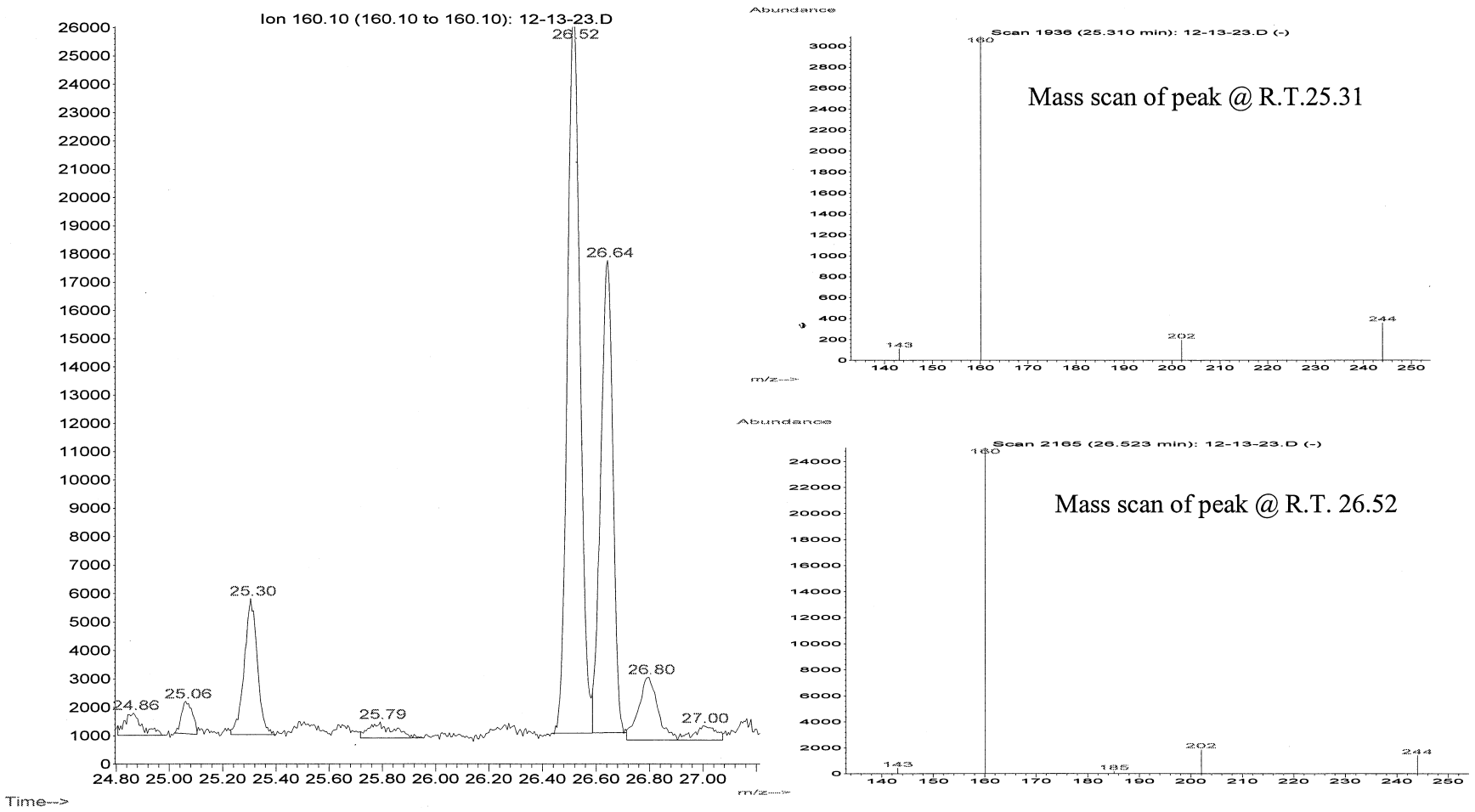

Figure 5. (a) SIM and monitor mass ratio (right panels) of peaks for 1,2-naphthoquinone-d0 and 1,4-naphthoquinone-d0 (as acetylated derivatives) in an ambient air sample collected by the XAD-4 bed from Lake Arrowhead, CA on 23 September 2002. The peaks selected showed similar retention times and monitor mass ratios compared with the standards in Figure 6a. (b) SIM & monitor mass ratio (right panels) of peaks for 9,10-phenanthraquinone-d0 and 9,10-anthraquinone-d0 (as acetylated derivatives) in an ambient air sample collected by the XAD-4 bed from Lake Arrowhead, CA on 23 September 2002. The peaks selected showed similar retention times and monitor mass ratios compared with the standards in Figure 6b. No 9,10-phenanthraquinone-d0 was detected in this sample. *(Continued)*

(b) LAH020923-XAD (SIM & SCAN)

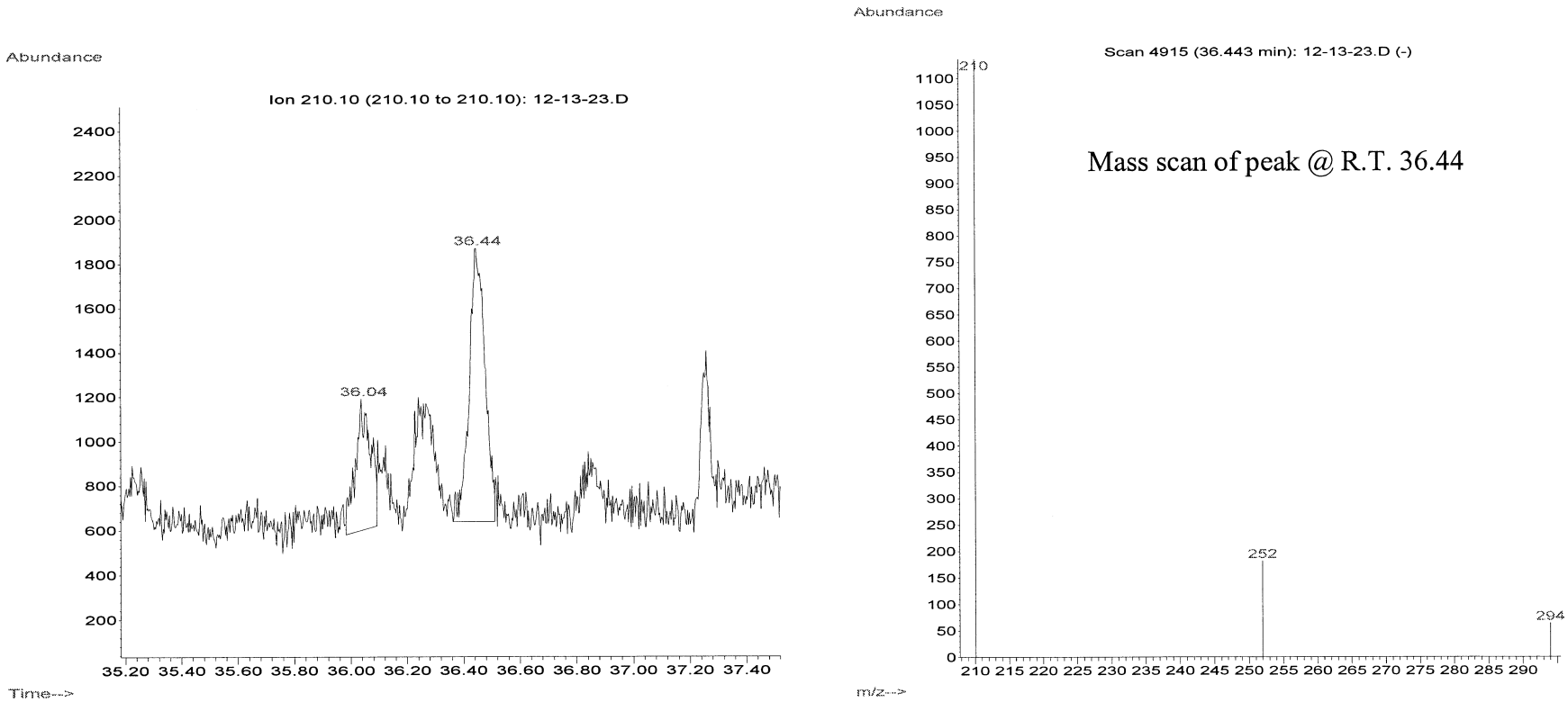

Figure 5. (Continued)

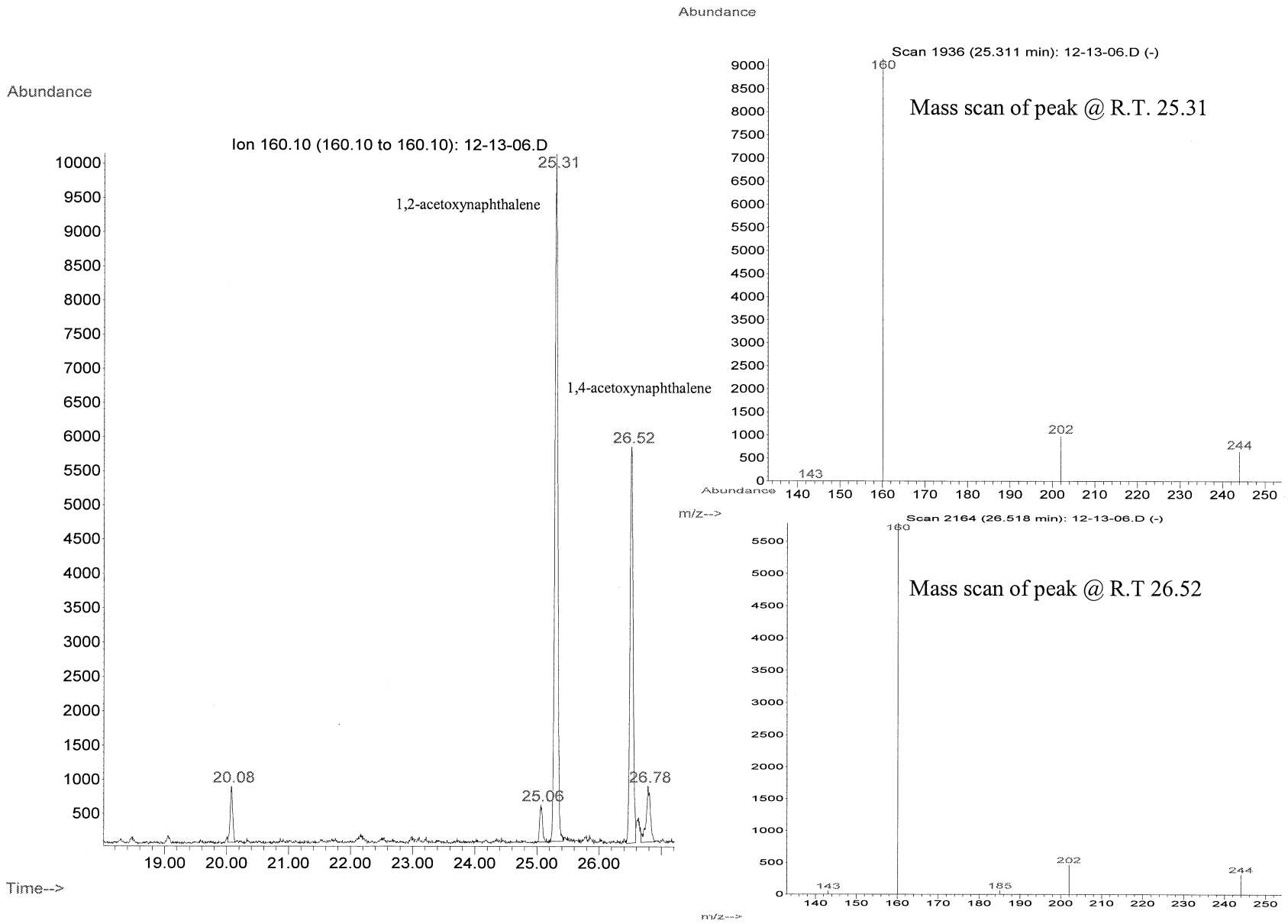

Figure 6. (a) SIM and monitor mass ratio (right panels) of of standards 1,2-naphthoquinone-d0 and 1,4-naphthoquinone-d0 (as acetylated derivatives). (b) SIM and monitor mass ratio (right panels) of of standards 9,10-phenanthraquinone-d0 and 9,10-anthraquinone-d0 (as acetylated derivatives). *(Continued)*

(b)

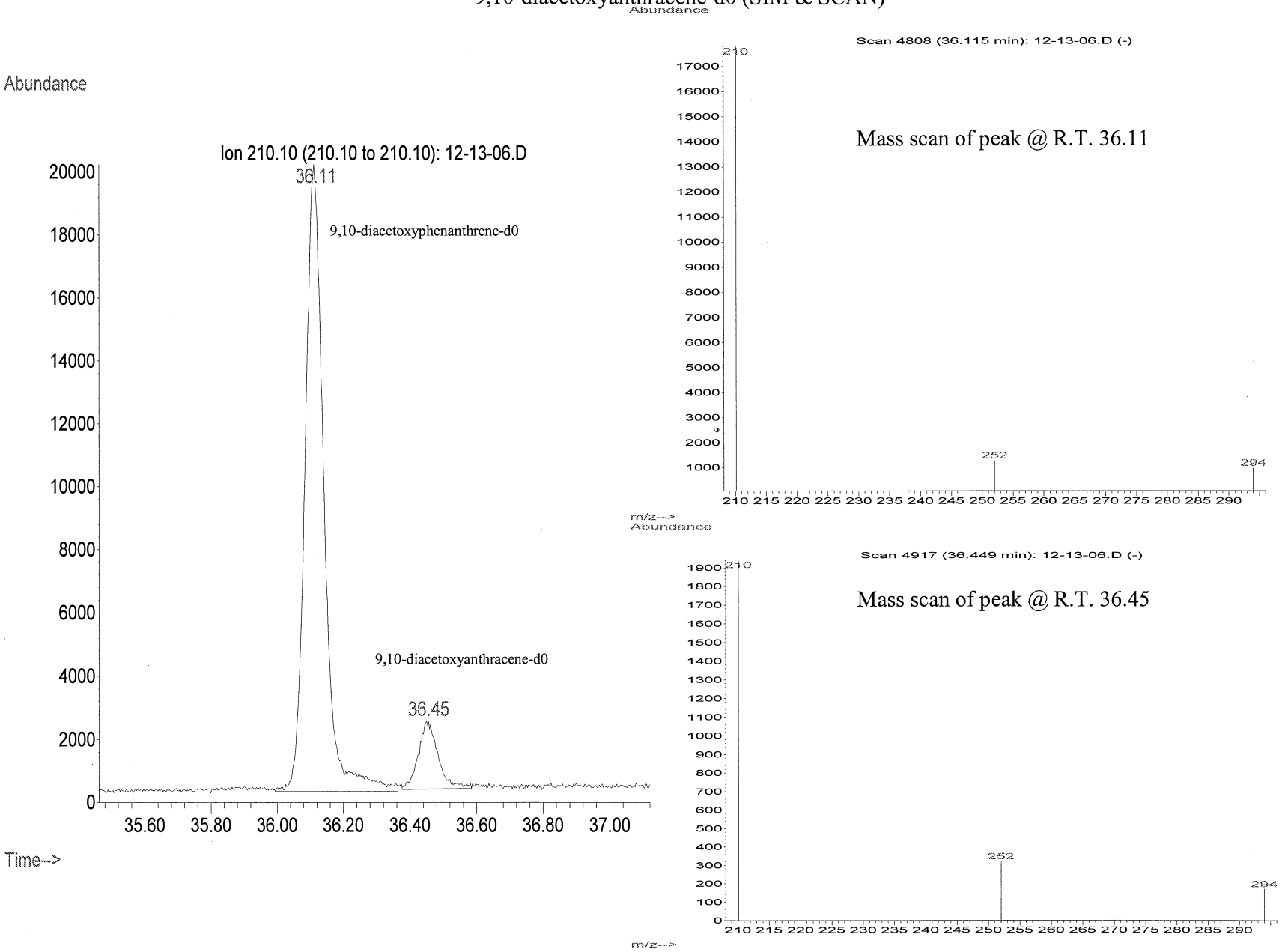

Figure 6. (Continued)

downwind of Los Angeles also showed elevated levels of 1,4-NQ and 9,10-PQ. Seasonal variability likely plays a role in the observed variation in ambient levels. Additional sampling is currently underway to address this issue. The analytical method developed in this study is presently being applied to the determination of quinones at 14 different sites in Southern California with linkages to ongoing health effects investigations.

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