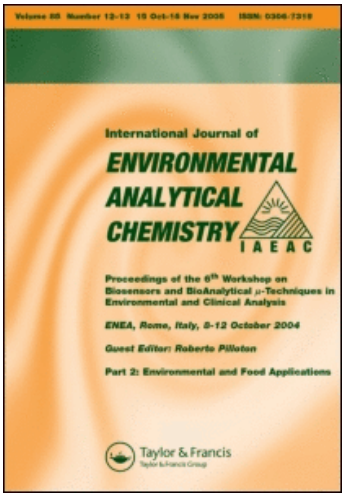

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ANALYTICAL METHOD DEVELOPMENT OF LONG-CHAIN KETONES IN $PM_{2.5}$ AEROSOLS USING ACCELERATED SOLVENT EXTRACTION AND GC/FID/MSD

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An analytical method has been developed to determine long-chain *n*-alkan-2-ones (C_{10}–C_{33}) in atmospheric particulate matter. This involves (1) solvent extraction with a Dionex Accelerated Solvent Extractor (ASE 200), followed by nitrogen blowdown; (2) a clean-up procedure using silica-gel chromatography to separate fractions of different polarities; and (3) gas chromatography with mass-selective detector (GC/MSD) identification and gas chromatography with flame ionization detector (GC/FID) quantitation. The recovery rates in the extraction/blowdown steps were quantified at different extraction and blowdown temperatures. The maximum recoveries for the selected ketones, obtained at 40°C for both extraction and blowdown, are 70–100% for the extraction step and 92–101% for the combined steps of blowdown and silica gel separation depending on the chain length of the ketones. The overall analytical instrumental detection limits for the ketones are $< 0.24\,ng/\mu L$ in the GC/FID.

Keywords: Aerosols; Long-chain ketones; Accelerated solvent extraction; GC/FID/MSD; Method development

INTRODUCTION

Relatively extensive studies have focused on the carbonaceous components of aerosols, particularly the nonpolar organic compounds, e.g. [1–5], for various reasons, ranging from potential climate impact, visibility reduction, to health impact [6,7]. However, studies on polar organics in aerosols are more limited [8–14]. This is due in part to the difficult and often labor-intensive analytical methods involved in analyzing and detecting the polar organic compounds. In particular, only a few studies have addressed and published qualitative or semiquantitative results of one class of the polar compounds, the long-chain ketones especially *n*-alkanones, in aerosols [13,15,16]. Some studies show that the ketones, like other classes of polar organic compounds, are oxidative or microbial products of aliphatic lipids, e.g. microbial formation from

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n-alkanes in the α-position [11,14]. These ketones may also come from different sources, such as remote forested areas by direct emission from higher plant waxes [13,15–18], biomass combustion [19,20], urban areas [21], and cooking smoke [22–24], of both biogenic and anthropogenic origins. Their presence is an indication of the influence of emission sources and atmospheric chemical processes on the composition of ambient aerosol particles. The aliphatic ketones in aerosols can therefore serve as tracers for the sources and processes involving organic carbon in aerosols when coupled with receptor models.

The lack of published data on the long-chain aliphatic ketones in the ambient aerosol particles is partly due to the fact that analytical methods, particularly sample extraction and handling processes, have not been well established. Rare studies reported the recovery rates of the aliphatic ketones from samples due to the often difficult and laborious sample extraction and handling procedures [25]; hence, it is difficult to judge the quality of the published results. Improved technologies, however, have now made it possible to quantify such important analytical parameters. For example, the accelerated solvent extractor (ASE; Dionex Co, USA), an automated system for extracting organic compounds from a variety of solid and semisolid samples, was first described in 1995 [26,27] and has been improved in the last few years. Compared with conventional solvent extraction, the solid or semisolid samples can be extracted using the ASE at elevated temperatures and pressures in short periods of time and with small quantities of solvents to obtain equivalent extraction results [28].

In this article, we describe an analytical method that was developed to determine the concentrations of long-chain aliphatic ketones in ambient aerosols. The method uses a combination of automated extraction and blowdown methods, using an ASE and blowdown instrument, Turbo Vap II (Zymark, USA), with a silica gel chromatography method to fractionate the extract into fractions of different polarities, and using different GC columns to analyze the ketones. This method is tuned for the detection of the long-chain aliphatic ketones from C_{10} to C_{27} at optimal solvent extraction and blowdown temperatures.

EXPERIMENTAL

Standards

Fourteen authentic standard compounds used in this study were purchased from Sigma-Aldrich. Of these, 13 were used as external standards: 2-decanone (2-C_{10}), 2-undecanone (2-C_{11}), 2-dodecanone (2-C_{12}), 2-tridecanone (2-C_{13}), 3-tetradecanone (3-C_{14}), 2-pentadecanone (2-C_{15}), 2-hexadecanone (2-C_{16}), 2-heptadecanone (2-C_{17}), 2-octadecanone (2-C_{18}), 2-nonadecanone (2-C_{19}), 10-henecosanone (10-C_{21}), 10-tricosanone (10-C_{23}), 14-heptacosanone (14-C_{27}). Deuterated *n*-tetracosane (*n*-tetracosane-d_{50}) was used as an internal standard.

ASE Extraction

Extractions of all test and field filter samples were performed on the ASE (ASE 200, Dionex Co.). Stainless steel extraction cells with a volume of 22 mL (Dionex Co.) were used. These have cellulose filters (Dionex Co.) at the outlet of each cell to contain

potential debris from the samples when the extract is transferred into a collection vial (40-mL gradient vials, Dionex Co.) after the extraction.

From the limited reports on organic matter extracted from soils [29,30] and aerosols [31], the results showed that changing the extraction pressure in a certain range does not appear to significantly affect the extraction [32]. Therefore, for this work, a 1500 psi pressure was chosen based on previous work [29,31].

Five extraction methods were chosen and tested to arrive at an optimized method for extracting the *n*-alkan-2-ones. For all five methods, static time was 5 min, flush volume was 60%, cyclic was 2, purge time was 60 s, air pressure was 100 psi, and nitrogen pressure was 150 psi. The solvent mix also remained the same at a dichloromethane (DCM) : methanol ratio of 3 : 1 (v/v). The five methods were different with respect to extraction temperature and preheating time. Samples were extracted at 40, 80, 120, 160, and 200°C with preheat times of 5, 5, 6, 8, and 9 min, respectively.

Concentration Using a TurboVap II

The extracts from ASE and separated fractions from chromatography were then automatically blown down to 0.5 mL using a TurboVap II (Zymark). Nitrogen was produced by a nitrogen generator (model N2-2010- (75–86), Whatman). Both the operating pressure and the outlet pressure of the nitrogen generator were 75 psi. The operating pressure of the TurboVap was 6 psi. The nitrogen flow was 10 L/min for the six cells. Under these conditions, the minimum purity of the nitrogen from the generator was 99.5%.

Separation (Clean-up)

Concentrated extracts from ASE/TurboVap were transferred into a vial of 5-mL volume and dried in a desiccator at room temperature. One milliliter of *n*-hexane was added to the vial and agitated carefully to redissolve the extracts. A glass chromatography column (10 mm i.d., Alltech Associates Inc.) was packed with the activated silica gel (at 130°C for 18 h). Glass wool (pesticide grade, Alltech Associates Inc.) was placed at both ends of the silica gel column to protect the silica gel from moving. The separation of the extracts was based on the polarity of different organic compounds. The nonpolar fraction containing saturated hydrocarbons was eluted by using 25 mL of *n*-hexane. The second fraction of low polarity, containing mainly PAH, was eluted with 25-mL of *n*-hexane and DCM mixture (6 : 4, v/v) [33]. The third fraction, of medium polarity and containing ketones and esters, was eluted with 25 mL of DCM and acetone (4 : 1, v/v) mixture. The last fraction, mainly containing alcohols and alkanoic acids, the most polar of the four fractions, was eluted with 25 mL of methanol.

Gas-chromatographic Identification and Quantification

The analyses of final concentrated fractions were performed on an Agilent 6890 GC/FID and an HP 5890 series II GC with the HP 5972 MSD (Hewlett-Packard), respectively. Identification of unknown compounds and confirmation of the compounds with the standards were carried out on the GC/MSD, and the quantification was carried out on the GC/FID.

GC/FID Analysis

Samples were injected onto the column using an automatic sampler (HP 7673, Hewlett-Packard) on the GC/FID. A 2-μL volume was injected in the splitless mode with a 1-min purge. Three different capillary columns were used to give an unequivocal identification [34].

The first capillary column was a ZB-WAX (100% polyethlene glycol, Phenomenex), 60 m × 320 μm i.d. × 0.50 μm film thickness. The initial oven temperature was 60°C and was held for 1 min. The oven temperature was programmed to increase to 265°C at 8°C/min and was held at this temperature for 20 min. The inlet temperature was kept at 250°C, and the carrier gas (He) flow was 2.0-mL/min constantly. The detector was kept at 270°C with hydrogen flow maintained at 40 mL/min and airflow at 450 mL/min.

The second column was a DB-FFAP, 30 m × 250 μm i.d. × 0.25 μm (J & W Scientific). The initial oven temperature was 50°C; this was then programmed to rise to 240°C at a rate of 6°C/min and held for 40 min. The flow of the carrier gas was 2.0 mL/min. Other conditions were as same as the first column.

The third column was a DB-5ms, 30 m × 250 μm i.d. × 0.25 μm (J & W Scientific). The initial oven temperature was set at 50°C and was held for 1 min. The oven temperature was programmed to rise to 290°C at a rate of 8°C/min and then held for 20 min. The temperature of the inlet was maintained at 280°C, and the temperature of the detector was maintained at 310°C. The flow of the carrier gas was 1.5 mL/min. Other operating conditions were the same as above.

GC/MSD Analysis

Samples were injected onto the column using an automatic sampler (Agilent 6890 Series) on the GC/MSD. The flow rate for each column was set to 1.5 mL/min to keep acceptable vacuum conditions. Other conditions were as same as for the GC/FID.

Blanks and Quality Control

Three groups of blank samples were prepared and analyzed. First, solvent blanks were used to test the contamination during the ASE performance at five different temperatures and during the entire procedure. Second, filter blanks were used to test possible contamination from filters during the analysis. The third sample blanks were handled in the same way as for the real samples with exposure to air for several minutes to test contamination from sampling. These filters were analyzed as described above. One control sample was analyzed every 12 samples to test the instrument condition.

RESULTS AND DISCUSSION

Calibration Linearity

The calibration curves of the compounds on the GC/FID and the GC/MSD were obtained using standards at 10 concentration levels ranging from 0.2 to 120 ng/μL. The GC/FID responses were highly linear within the concentration range. For the five selected *n*-alkanones ranging from C_{13} to C_{19}, the correlation coefficients (r^2) of the response *versus* concentration were between 0.99971 and 0.99987 using ZB-WAX,

between 0.99912 and 0.99935 using DB-FFAP, and between 0.99540 and 0.99671 using the DB-5ms column. The linear calibration curves were from 0.2 to 120 ng/μL for the ZB-WAX and for the DB-FFAP, and from 0.2 to 80 ng/μL for the DB-5MS column. The concentrations of the individual ketones in ambient samples were between 0.2 and 30.0 ng/μL, which were within the working calibration curve ranges.

Although the response and linearity of ketones using the ZB-WAX column were better than those using the DB-5ms column in the GC/FID, the ZB-WAX column was not suitable for use on the GC/MSD because of its high bleeding amount, which significantly increases the MSD background signals, flooding the signals from the compounds. However, the DB-FFAP capillary column has a very low bleeding amount and is suitable for the use on the GC/MSD.

Analytical Reproducibility

To assess the analytical reproducibility on the GC/FID by using the three columns, six replicate analyses of extracts, containing five selected ketones (2-C_{13}, 2-C_{15}, 2-C_{16}, 2-C_{17}, and 2-C_{19}) at two concentration levels, were carried out on the ZB-WAX, the DB-FFAP, and the DB-5ms columns, and the relative standard deviations (RSD) of the responses from each injection at two levels were measured. In the high concentration range, 80 ng/μL, the RSD for the five selected ketones were consistent between 0.4 and 0.5% using the ZB-WAX column. However, for a lower concentration of 20 ng/μL, the RSD were more variable from 0.6 to 2% among the ketones using the same column (Table I). For the DB-FFAP column, there was a similar situation, with the RSD varying less for the higher concentration than for the lower concentrations. For the DB-5ms column, the RSD were higher than the two polar columns, and a different pattern emerged. The RSD were more consistent at a lower concentration, between 2.4 and 2.5% at 20 ng/μL, but varied from 2.6 to 4.0% at 80 ng/μL (Table I).

TABLE I Comparison of relative standard deviations (RSD %) of target long-chain ketones in different concentrations (ng/μL) on the GC/FID using three capillary columns

Ketone	*ZB-WAX*				*DB-FFAP*				*DB-5MS*			
	80[a]	*20*[b]	*0.24*[c]	*0.12*[d]	*80*[a]	*20*[b]	*0.12*[c]	*0.06*[d]	*80*[a]	*20*[b]	*0.12*[c]	*0.06*[d]
2-C_{10}	n.a.	n.a.	2.5	2.8	n.a.	n.a.	1.4	4.8	n.a.	n.a.	11.7	19.4
2-C_{11}	n.a.	n.a.	2.2	10.6	n.a.	n.a.	0.4	0.5	n.a.	n.a.	10.6	13.6
2-C_{12}	n.a.	n.a.	3.3	3.4	n.a.	n.a.	1.7	1.0	n.a.	n.a.	10.0	13.6
2-C_{13}[e]	0.5	2.0	3.7	1.8	1.6	0.9	1.6	16.5	4.0	2.5	5.7	28.1
3-C_{14}	n.a.	n.a.	1.2	1.6	n.a.	n.a.	0.9	2.9	n.a.	n.a.	7.9	18.2
2-C_{15}[e]	0.4	0.6	3.9	1.1	1.7	1.0	0.8	3.7	3.5	2.5	3.4	26.4
2-C_{16}[e]	0.4	0.7	15.9	10.7	1.6	1.6	2.3	0.6	3.2	2.5	3.2	20.4
2-C_{17}[e]	0.4	0.6	11.0	23.1	1.6	1.1	1.5	0.6	3.0	2.5	4.4	28.0
2-C_{18}	n.a.	n.a.	17.0	15.0	n.a.	n.a.	0.5	2.6	n.a.	n.a.	4.5	21.9
2-C_{19}[e]	0.4	0.9	13.0	23.3	1.6	1.1	1.5	2.3	2.6	2.4	8.5	27.8
10-C_{21}	n.a.	n.a.	18.6	17.3	n.a.	n.a.	1.8	0.9	n.a.	n.a.	11.6	19.8
10-C_{23}	n.a.	n.a.	12.0	24.6	n.a.	n.a.	14.1	5.3	n.a.	n.a.	7.4	23.9
14-C_{27}	n.a.	n.a.	8.7	28.4	n.a.	n.a.	4.0	25.7	n.a.	n.a.	8.0	12.5

[a]High concentration. [b]Lower concentration. [c]Second lowest level of concentration. [d]Lowest concentration. [e]Selected ketones for getting optimization methods on ASE, blowdown and analytical reproducibility. n.a., not available.

Instrument Detection Limit

The instrument detection limit (IDL) is defined as two times the signal-to-noise ratio and with the RSD lower than 20% [34]. The RSDs varied with the compounds at any given concentration. Table I shows the RSDs for different concentrations for the three columns used. At the second lowest concentrations (0.24 ng/μL for ZB-Wax column, and 0.12 ng/μL for both DB-FFAP and DB-5MS columns), all RSDs were $<20\%$, and the signal-to-noise ratios were 6, much higher than 2. Hence, these concentrations were determined as the IDLs for all ketones listed in Table I. The method detect limit (MDL) in aerosol samples is measured by the final air volume of each sample and the injection volume of sample extracts into the columns. For a typical air volume of 500 m^3 using a high-volume sampler over 8 h, and a final volume of 20 μL, the MDL for the ketones will be 0.8 pg/m^3 if either the DB-FFAP or DB-5MS column is used.

Extraction Optimization

The extraction process is the most critical step in the recovery from the filter samples before analysis, and because the recoveries impact on the accuracy of results, considerable effort was spent on quantifying the recoveries. To optimize the recovery method for the ketones using the ASE, we focused our work on three factors that determine the recoveries, namely, extraction temperature, different levels of the analytes in substrates, and the difference in the individual compounds.

First, the impact of the extraction temperature on the recovery was examined. The tests were carried out at 40, 80 and 120, 160, and 200°C, respectively. For each temperature, two groups of six filters each were spiked with 30 and 60 μg of each ketone, respectively, and were extracted. The extracts then were concentrated by blowdown to 1 mL using the TurboVap II at 40°C, and analyzed on the GC/FID using the ZB-WAX column.

The results showed that the average recoveries of the selected ketones from C_{13} to C_{19} were similar at temperatures of 40, 80, and 120°C but were lowest at 200°C for the high (60 μg) spike level (Fig. 1). The low (30 μg) spike level showed the same result. With the exception of the C_{13} ketone, the recoveries appear to decrease with the extraction temperature, so part of the reason for this drop may be the thermal decomposition of the compounds or the increased volatility while the temperature was above 120°C, although the RSD for the recoveries improve at the higher temperatures. At 200°C, the recoveries for all ketones dropped substantially to $<50\%$.

To further explore the dependence of the recovery rates on the levels of the ketones, the amounts of ketones spiked onto filters were 4 and 20 μg for each compound. The spiked filters were extracted at 40°C, as mentioned above. Figure 2 presents, for the four different spike levels, the recoveries of C_{19}, which is the less volatile compound in the group of the selected ketones. The results were essentially the same at the same extraction temperature and two blowdown temperatures (30 and 40°C). However, for the rest, the recoveries of 4-μg level spiking samples were lower than those of 20-μg level spiking samples. This indicates that the recoveries were not dependent on the level of ketones in the sample substrate when the compounds were low volatile. It should be noted that these recoveries of volatile ketones were clearly affected by the blowdown temperature, which was investigated further, and the results are

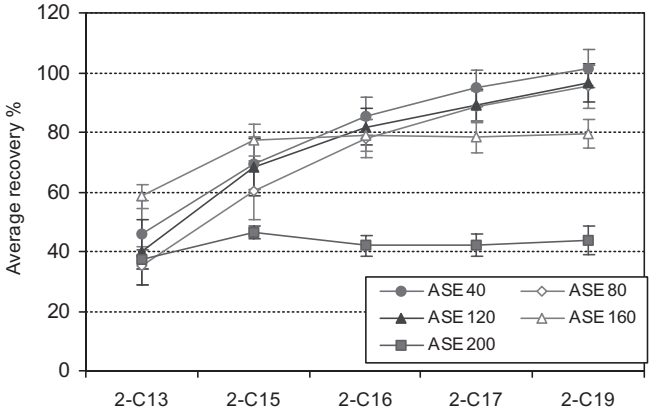

FIGURE 1 Average recoveries and relative standard deviation of the selected ketones with ASE extraction and TurboVap blowdown at 40°C for a 60-μg spike level.

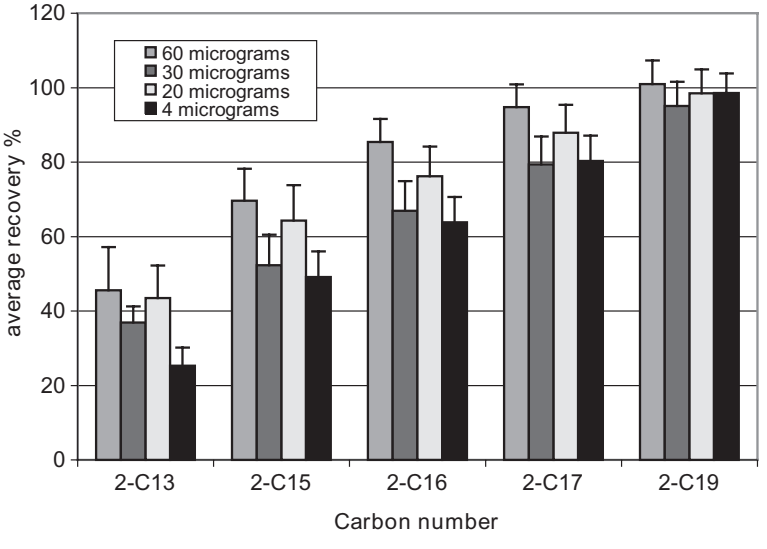

FIGURE 2 Average recoveries and relative standard deviation of the selected ketones with the ASE extraction at 40°C. 60- and 30-μg spiked samples were blowndown at 40°C, and 4- and 20-μg spiked samples were blown down at 30°C.

presented in the following section. Concerning the factors discussed above, 40°C was chosen as our optimal operating temperature for the extraction of the ASE.

Blowdown Optimization

In this study, the blowdown was carried out using the TurboVap II. Because the organic components usually have some saturation vapor pressures, the blowdown will lead to losses of the solutes as well. Hence, it is critical to determine how the concentration procedure impacts on the recoveries of the ketones. Again, one of the controlling factors is the blowdown temperature of the extract, controlled by

the water bath in the TurboVap II. The higher the blowdown temperature, the faster the blowdown is achieved; however, larger losses are likely to result due to increased volatilities of the ketones at higher temperatures.

Other factors that should have an impact are the N_2 flow rate and the operating pressure, and solvent properties discussed below; however, we kept the flow rate and operating pressure constant, as recommended by the manufacturer throughout the study, and hence cannot assess the impact of both factors. We did find that at the recommended N_2 flow rate and operating pressure, the recoveries were sufficiently high (more than 80%) for the ketone measurements if the carbon number was higher than 16.

Figure 3 shows the recoveries of the ketones for the spike level of 60 μg at blowdown temperatures of 30 and 40°C. For all ketones except C_{19}, the recoveries were lower at 40°C than at 30°C. This reduction was dependent on the carbon number in the compounds, decreasing with increasing carbon number. The reduction was most pronounced for 2-tridecanone, with a substantial decrease from 68 to 48%. In contrast, the recovery of the 2-nondecanone was close to 100% at both temperatures, suggesting that it was not very dependent on the blowdown temperature.

The reduced recoveries at the higher temperature of 40°C are a reflection of the losses of higher volatility compounds during blowdown. The volatility is dependent on the saturation vapor pressure, which decreases with carbon chain length in the compounds but increases with temperature. Hence, with increasing carbon chain length, the volatility is decreased, and the effect of temperature is correspondingly reduced.

The relationship of recoveries *versus* carbon chain length is essentially the same for the blowdown step only and when both the extraction (at 40, 80, and 120°C) and blowdown steps were combined (Figs. 1 and 3), although with the combined steps, the recoveries are slightly lower than the blowdown step only. The same relationship indicates that the loss of the ketones in the extraction and blowdown was mostly due to the blowdown step, with minor contributions from the extraction step of $< 10\%$. Furthermore, the contribution from the extraction step was uniform with different carbon chain lengths. Hence, it is desirable to reduce the loss of the ketones from the extracts during the blowdown step by keeping the blowdown temperature low. The

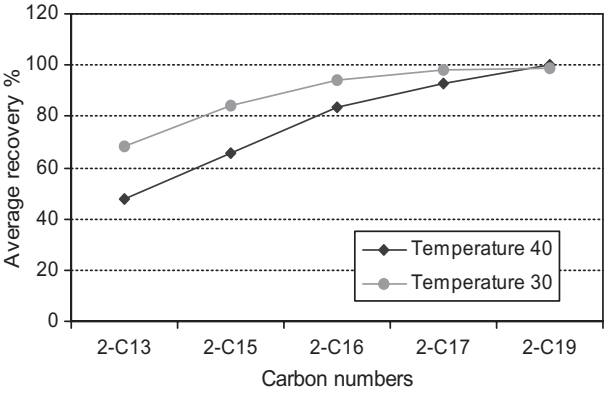

FIGURE 3 Average recoveries of the selected ketones at two blowdown temperatures using Turbo Vap II for a 60-μg spike level.

optimized blowdown temperature of 30°C or lower must be used. This will necessarily increase the blowdown time but will ensure higher recoveries.

Recovery During Silica-gel Chromatographic Separation

Clean-up or separation procedures may help to isolate the analytes from coextracted sample material that may interfere with the analysis [34]. To evaluate recoveries in the separation procedure, two levels, 4-μg and 40-μg ketones in 1 mL of solutions, were used. The solutions were dried in the desiccator and then separated using the silica-gel chromatography using the aforementioned method. Figure 4 shows the average recovery distributions of ketones ranging from C_{10} to C_{27}. The recoveries were 47–100.7%, varied with the carbon numbers, and were similar for the two concentrations. The recoveries of the five ketones from C_{13} to C_{19} were 92–100%, which indicated that a high efficacy was obtained to isolate ketones using the silica-gel liquid chromatography, and the recoveries were independent of concentrations.

The separation steps included silica-gel separation and the blowdown procedure. Comparing the recoveries of ketones during the separation step with those during the blowdown step, higher recoveries were obtained from the separation steps. The blowdown procedure is also affected by the solvent property. Two different solvent mixtures were used in the separation and blowdown. The solvent mixture used in the separation was DCM : acetone (4 : 1, v/v), and that in blowdown was DCM : methanol (3 : 1, v/v). Because methanol has a higher boiling point than other solvents, it is more difficult to evaporate.

Contaminants in Blanks

Blanks posed another challenge with measurements for ketones, especially at low levels. Three groups of blank samples such as solvent, filters, and filter samples were analyzed. The analysis showed no target compounds in the solvent blank extracts using the ASE at the five temperatures and the silica-gel chromatographic separation step. Other contamination compounds, both phthalates and unidentified compounds, increased with

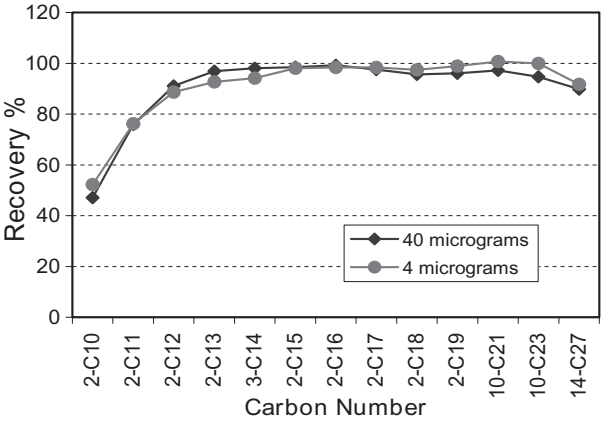

FIGURE 4 Average recoveries of all target ketones during the separation step and blowdown step with a 30°C water bath and a DB-FFAY column.

the temperatures of the ASE operations. Trace ketones ranging from C_{15} to C_{18} were detected by GC/FID and GC/MSD in extracts from filter blanks and sample blanks using the complete method. These ketones found in the blanks may be present in the bonding materials of the quartz filters or may arise from bacteria activity [15]. Hence, for all filter results, the sample blank results that included the contributions from the ketones were subtracted from the sample data.

Recovery of Using the Validation Method

The ketone recoveries of three level spiked filters using the validation method are presented in Fig. 5. This shows that the optimized conditions yielded high recoveries (80–100%) for the QA filters from the validation method for the ketones when the carbon number was above C_{17} at three levels; the recoveries decreased slightly with the spiked level when the carbon number was below C_{17}. The ketones with the carbon number higher than C_{17} have a low volatility or nonvolatility, so they lose less during the blowdown process, and data showed no loss during the silica-gel separation. However, the ketones with a lower carbon number (less than C_{17}) have a volatility that increases with decreasing carbon number, and therefore they were lost during the blowdown step at the same spiked level. The recoveries of the same carbon number ketones $< C_{17}$ were slightly reduced from high spike level to low spike level, because the lower spike level required a smaller final volume for analysis and a longer blowdown process. Recoveries of ketones with a carbon number below C_{14} were low, making their quantitative data less accurate.

Analytical Precision

The analytical precision was measured by the relative standard deviation (RSD) of the recovery for each target compound from six duplicated spiked filters at three levels (0.4, 4, and 20 μg), using the validation method. The RSD data are shown in Fig. 5. For both 4- and 20-μg spike levels, the RSDs were 4–9% for C_{10} to C_{27} ketones. The RSDs of lowest level (0.4 μg) were 3–8% for all ketones except 3-C_{14} (13%). Therefore, the analytical precision using the method is relatively high.

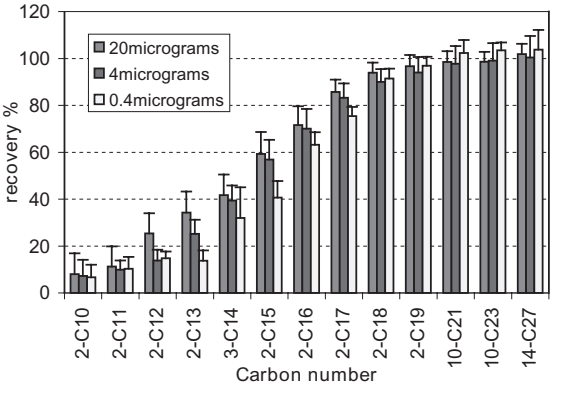

FIGURE 5 Average recoveries and precisions of the target ketones for three level spiked filters using the method validation.

Application of the Method

The analytical method presented above is reliable, accurate, and practical for analyzing long-chain ketones, especially C_{14} to C_{27}, in fine aerosols. This method can be used to measure various amounts of the ketones in aerosols from trace to high levels with the wide range of the working calibration curves obtained, and with a comparable high recovery efficiency and precision for the entire method and even with each step. This method was applied to $PM_{2.5}$ samples collected from two urban sites in downtown Toronto. $PM_{2.5}$ aerosol samples were collected on quartz filters from the two sites using a semihigh-volume sampler at a flow rate of 490–615 L/min. Long-chain ketones including *n*-alkan-2-ones ranging from C_9 to C_{33} and 6,10,14-trimethylpentadecan-2-one (C_{18i}) were measured in the aerosols. The results showed that airborne concentrations of the individual *n*-alkan-2-ones were 20–600 pg/m^3, and their homologue distributions *versus* carbon numbers, carbon preferential index, and ratio of 6,10,14-trimethylpentadecan-2-one (C_{18i}) to 2-octadecanone (C_{18}) were sensitive to their source impacts.

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