Application Note: 493

Quantitative Analysis of Environmental Air Contaminants Using APCI-MS/MS in Mobile Laboratories

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Key Words

- **Environmental Monitoring**
- **TSQ Series Triple Quadrupole MS**

Introduction

There are many potential hazards in our environment. Chemical emissions, accidental chemical spills and fires are of particular concern. A real-time analytical atmospheric pressure chemical ionization-tandem mass spectrometry (APCI-MS/MS) method for the quantitative analysis of air contaminants has been developed using a customized, direct-sampling APCI device coupled with a Thermo Scientific TSQ series triple stage quadrupole mass spectrometer. This method is critical for both environmental monitoring in areas of steady or long-term exposure and also for accidental or emergency instances. In such situations, timely and accurate qualitative and quantitative information on the types and levels of various toxic chemical contaminants is required to evaluate the hazard and prevent public exposure. Methods have been developed for chemicals related to the ambient air quality criteria, governed by the Ministère du Développement durable, de l'Environnement et des Parcs (MDDEP) of Québec, Canada. Criteria are illustrated in Table 1, for a limited selection of contaminants. A TSQ Series triple stage quadrupole mass spectrometer, with a customized APCI device for direct sampling, has been used (Figure 1).

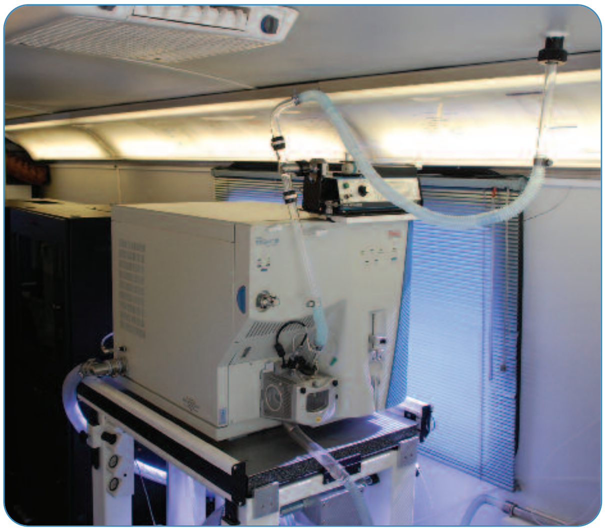

Figure 1: TSQ Series triple stage quadrupole with the ion source customized for direct air sampling.

Table 1. Ambient air quality criteria for common contaminants (limits of acceptance)

Compound	Limit Concentration (maximum mean/4 minutes) (µg/m³)	Limit of Detection (MS/MS) (µg/m³)
Acetone	8600	4
Acrylic acid	270	0.1
Ethyl-3-ethoxypropionate	300	0.02
Ethylacetate	20	16
Hydrogen chloride	1150	8
Methyl-ethyl ketone	740	6
Naphthalene	200	2
Phenol	160	0.4
Propylene glycol monomethyl ether (PGME)	ND	1
Sulfur dioxide	1050	0.3
Triethylamine	22	5

Goal

1) To develop a rapid, on-site, real-time air analysis method to identify and quantitate several common air contaminants.
2) To demonstrate the advantages of using the Thermo Scientific Ion Max source and tandem mass spectrometry (MS/MS) for the detection and determination of a selected range of atmospheric pollutants.
3) To establish and validate methods for air quality control programs, emission inventory and reporting, compliance and enforcement.

Experimental

Preparation of Standards

Standards were prepared by infusing saturated vapor of standard-grade samples of phenol, propylene glycol monomethyl ether (PGME), methyl-ethyl ketone (MEK), and ethylacetate, respectively into a flow of ambient air using a gastight syringe pumping system connected to the Ion Max™ source of the mass spectrometer (Figure 2). The concentrations of standards were calculated as a function of the infusion rate of saturated vapor of the respective standards into a non-contaminated, continuous flow of atmospheric air, drawn under normal conditions of temperature and pressure. See Tables 2 and 3.

$$Conc(ppb) = \frac{Ps}{Pa} \times \frac{I}{F} \times 1000$$

Ps = Vapor pressure of the compound (mm Hg at 21 ºC)

Pa = Atmospheric pressure (mm Hg at 21 ºC)

I = Infusion rate (µL/min)

F = Sampling pump flow (L/min)

$$Conc(\mu g/m^3) = Conc(ppb) \times \frac{W}{V}$$

W = Molecular weight of analyzed compound

V = Volume (24 liters at 21 ºC)

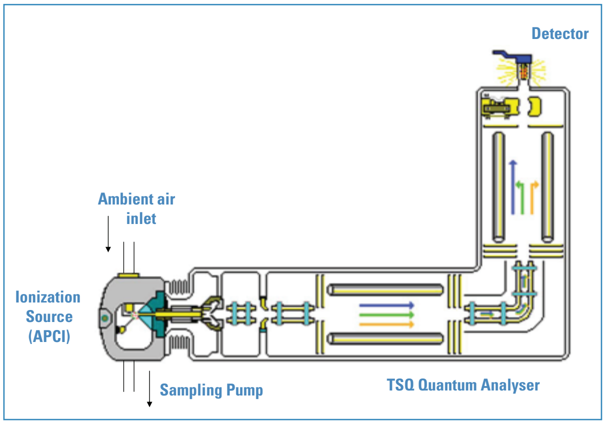

Figure 2: Block diagram of the TSQ Series triple stage quadrupole mass spectrometer custom source.

Table 3. Sample calculation of concentrations of compounds of interest.

	Phenol	**Ethylacetate**	**MEK**	**PGME**
Vapor pressure (Ps)	0.62	75.1	75.6	12
Syringe capacity (mL)	5	1	1	1
Speed setting	9	7	2	7
Infusion rate (µL/min)	1250	100	15	100
Sampling pump flow (L/min)	57	57	55	57
Molecular weight	94	88	72	90
Concentration (ppb)	18	173	27	28
Concentration (µg/m^3)	70	636	81	104

Sample Analysis

Air samples were drawn directly from open atmosphere into the Ion Max source housing through the built-in probe aperture. The set-up consisted of an infusion pump regenerative blower, with the drain tube of the source chamber serving as the outlet. Following APCI, the resulting ions entered the mass spectrometer through the ion transfer tube interface.

MS Conditions

Mass spectrometer:	Thermo Scientific TSQ Quantum Discovery MAX
APCI corona voltage:	4 kV (- 4 kV in negative ion mode)
Ion transfer tube temperature:	180 ºC
Skimmer offset:	5 V
CID gas pressure:	1.5 mTorr
Resolution:	Unit Resolution (0.7 FWHM)
Analytical scan type:	Selective reaction monitoring (SRM)
SRM conditions:	Scan time: 50 ms Scan width: 1.000 Da

The MS/MS experimental conditions for SRM are shown in Table 4.

Table 2. Calibration of the infusion pump (Correlation between syringe speed and infusion rate).

Syringe capacity	**Syringe speed**								
	1	2	3	4	5	6	7	8	9
	Flow rate (µL/min)								
10 µL	0.1	0.15	0.20	0.35	0.50	0.75	1.0	1.5	2.5
100 µL	1.0	1.5	2.0	3.5	5.0	7.5	10	15	25
1 mL	10	15	20	35	50	75	100	150	250
2.5 mL	25	38	50	88	125	188	250	375	625
5 mL	50	75	100	175	250	375	500	750	1250
10 mL	100	150	200	350	500	750	1000	1500	2500
50 mL	350	560	720	1230	1800	2560			

Table 4. MS/MS experimental conditions for SRM.

Compound	**Precursor Ion *(m/z)***	**Product Ion *(m/z)***	**Tube Lens Voltage (V)**	**Collision Energy (V)**
$^{13}C_2$-acetic acid	94	61	56	11
d_6-acetone	65	33	82	18
Ethylacetate	89	61	45	8
MEK	73	43	108	13
PGME	91	31	54	21
PGME	91	73	54	5
Phenol	126	93	35	13

Results and Discussion

In negative ion mode, $^{13}C_2$-acetic acid was used as an internal standard. Acetic acid produced a deprotonated molecule (*m/z* 94) $[^{13}CH_3{}^{13}COOH{\cdot}O_2]^-$ which, under CID conditions, produces CH_3COO^- (*m/z* 61). Phenol forms an analog adduct $[C_6H_5OH{\cdot}O_2]^-$ (*m/z* 126), which yields a product ion at *m/z* 93, $C_6H_5O^-$.

In positive ion mode, acetone-d_6 (*m/z* 65 to *m/z* 33) was used as an internal standard. Two precursor ion – product ion transitions were monitored, *m/z* 91 to *m/z* 31 and *m/z* 91 to *m/z* 73, respectively, in multiple reaction monitoring (MRM) mode for the analysis of PGME.

The limit of detection (LOD) is the concentration equivalent of 3x standard deviation of the response at the background level (i.e., ambient air, in the absence of the subject compound).

The calibration data for ethylacetate, MEK, PGME, and phenol are shown in Figures 3 through 10. The quantitative results are listed in Tables 5 through 8.

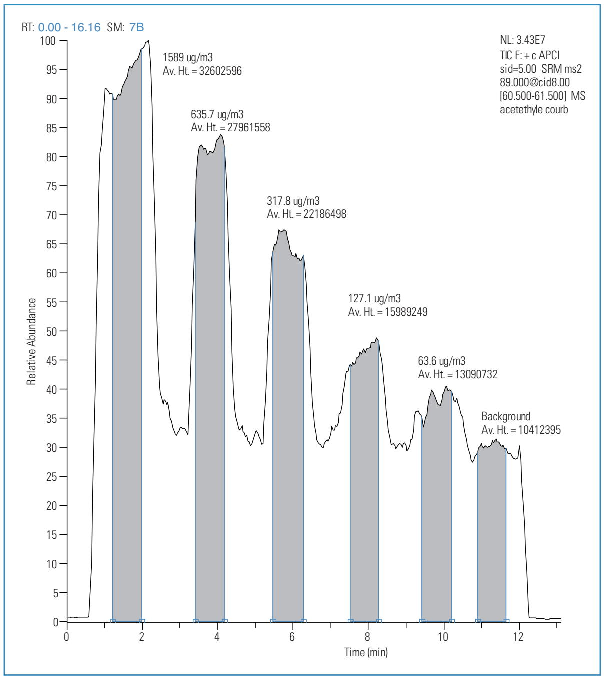

Figure 3: Reconstructed ion trace for ethylacetate to produce the calibration curve.

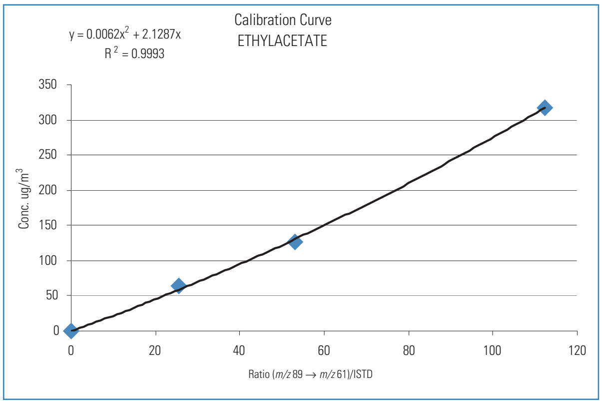

Figure 4: Calibration curve for ethylacetate.

Table 5. Quantitative results for ethylacetate and LOD determination.

ETHYLACETATE

ISTD: Acetone d_6, syringe 1 mL, Speed 2					
SRM (*m/z* 65→*m/z* 33)					
RT (min.)	Syringe Speed	Average Height	Background Subtracted		
10.5	OFF	26000			
15.55	2	130873	104873		

Ethylacetate						
SRM (*m/z* 89→*m/z* 61)						
RT (min)	Syringe Speed	Average Height	Background Subtracted	Response/ISTD Ratio	Concentration (µg/m³)	
1.2 - 2.0	9	32602596	22190201			
3.4 - 4.2	7	27961558	17549163			
5.5 - 6.3	5	22186498	11774103	112.3	317.8	
7.5 - 8.3	3	15989249	5576854	53.2	127.1	
9.4 - 10.2	1	13090732	2678337	25.5	63.6	
	OFF	10412395	0	0.0	0	Std. Dev. = 218065
		(3 x Std. Dev.) =	654194	6.24	16.2	**LOD**

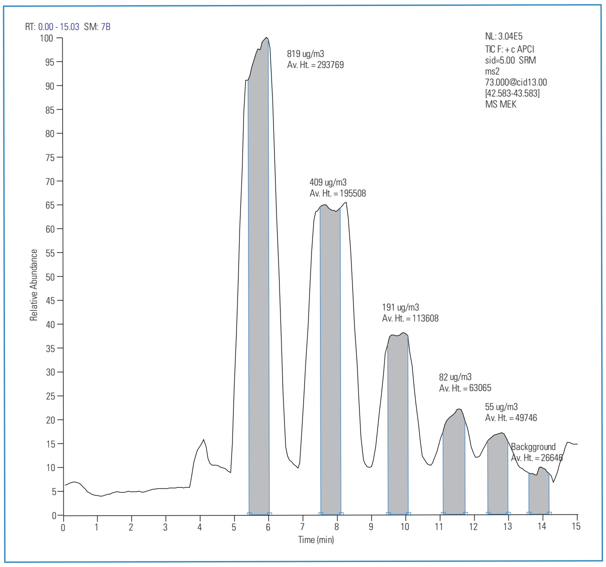

Figure 5: Reconstructed ion trace for MEK to produce the calibration curve.

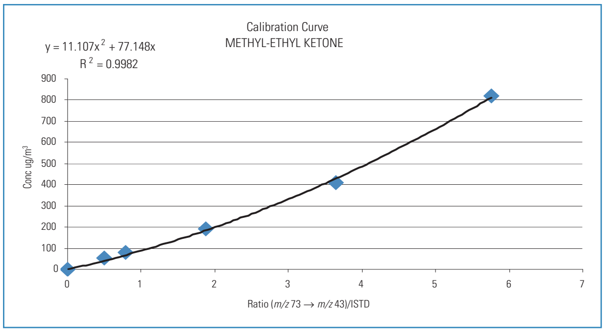

Figure 6: Calibration curve for MEK.

Table 6. Quantitative results for MEK, and LOD determination.

METHYL-ETHYL KETONE (MEK)

ISTD: Acetone d_6, syringe 1 mL, Speed 2					
SRM (*m/z* 65→*m/z* 33)					
RT	Syringe Speed	Aver Height	Background Subtracted		
3.03	OFF	45240			
2.38		91628	46388		

Methyl-ethyl ketone						
SRM (*m/z* 65→*m/z* 33)						
RT (min)	Syringe Speed	Average Height	Background Subtracted	Response/ISTD Ratio	Concentration (µg/m^3)	
5.4 - 6.0	9	293769	267123	5.8	819	
7.5 -8.1	7	195508	168862	3.6	409	
9.5 - 10.1	5	113608	86962	1.9	191	
11.1 - 10.7	3	63065	36419	0.8	82	
12.4 - 13.0	1	49746	23100	0.5	55	
13.6 - 14.2	OFF	26646	0	0.0	0	Std. Dev. = 1100
		(3 x Std. Dev.) =	3300	0.1	6	**LOD**

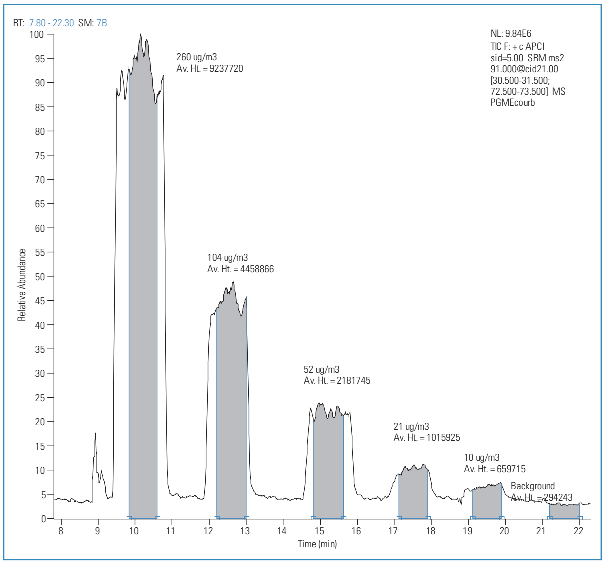

Figure 7: Reconstructed ion trace for PGME to produce the calibration curve.

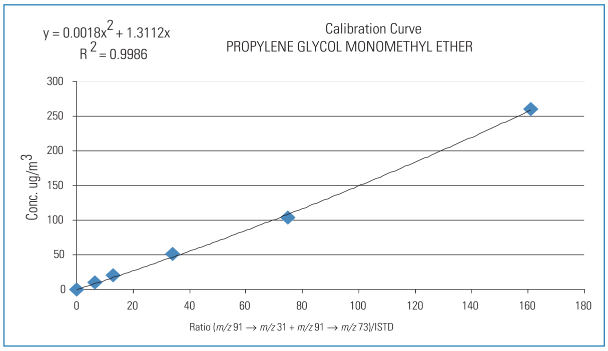

Figure 8: Calibration curve for PGME.

Table 7. Quantitative results for PGME, and LOD determination.

PROPYLENE GLYCOL MONOMETHYL ETHER (PGME)

ISTD: Acetone d_6, syringe 1 mL, Speed 2					
SRM (*m/z* 65→*m/z* 33)					
RT	Syringe Speed	Aver Height	Background Subtracted		
11.00	OFF	12500			
7.30		68039	55539		

Propylene Glycol Monomethyl Ether (PGME)						
MRM (*m/z* 91→*m/z* 33 + *m/z* 91→*m/z* 73)						
RT (min)	Syringe Speed	Average Height	Background Subtracted	Response/ISTD Ratio	Concentration (µg/m³)	
9.8 - 10.6	9	9237720	8943477	161.0	260	
12.2 -13.0	7	4458866	4164623	75.0	104	
14.8 - 15.6	5	2181745	1887502	34.0	52	
17.1 - 17.9	3	1015925	721682	13.0	21	
19.1 - 19.9	1	659715.5	365473	6.6	10	
21.2 - 22.0	OFF	294243	0	0.0	0	Std. Dev. = 15262
		(3 x Std. Dev.) =	45785	0.8	1	**LOD**

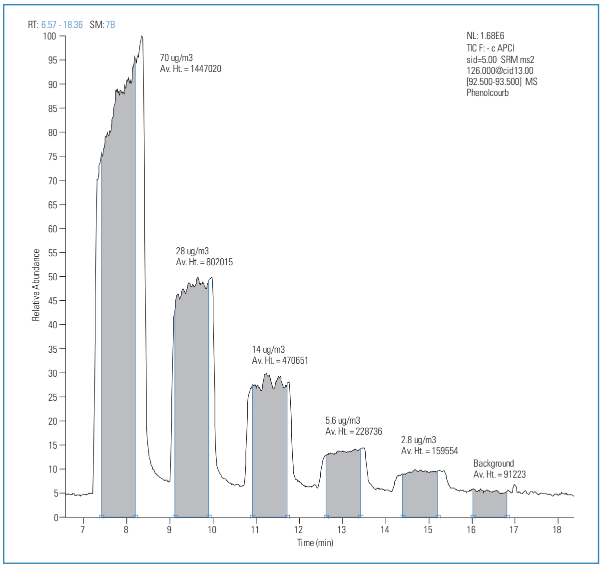

Figure 9: Reconstructed ion trace for phenol to produce the calibration curve.

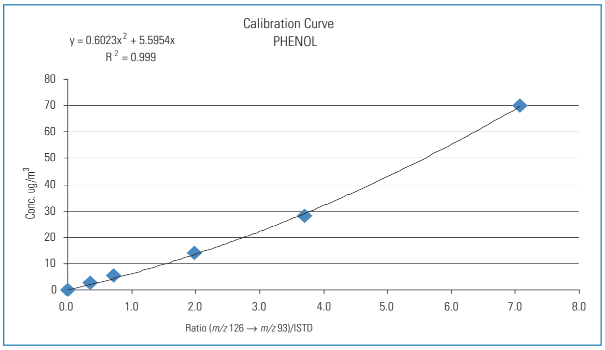

Figure 10: Calibration curve for phenol.

Table 8. Quantitative results for phenol, and LOD determination.

PHENOL

ISTD: Acetic acid $^{13}D_2$, syringe 1 mL, Speed 2					
SRM (*m/z* 94→*m/z* 61)					
RT	Syringe Speed	Aver Height	Background Subtracted		
6.0	OFF	57639			
4.6		249205	191566		

Phenol						
SRM (*m/z* 126→*m/z* 93)						
RT (min)	Syringe Speed	Average Height	Background Subtracted	Response/ISTD Ratio	Concentration (µg/m^3)	
7.4 - 8.2	9	1447020	1355797	7.1	70	
9.1 - 9.9	7	802015	710792	3.7	28	
10.9 - 11.7	5	470651	379428	2.0	14	
12.6 - 13.4	3	228736	137513	0.7	5.6	
14.4 - 15.2	1	159554	68331	0.4	2.8	
16.0 - 16.8	OFF	91223	0	0.0	0	Std. Dev. = 3871
		(3 x Std. Dev.) =	11613	0.06	0.4	**LOD**

Conclusion

The custom TSQ Series triple stage quadrupole mass spectrometer system allows the detection and quantitative analysis of a series of chemical pollutants in ambient air. Concentration of these pollutants can be determined in a real-time fashion for immediate action in case of chemical spills, fire, etc., or for the purpose of trending in environmental monitoring.

This application demonstrates that LODs can be achieved with the TSQ Series triple stage quadrupole mass spectrometer in real time, without sample pre-concentration or any separation technique. The achieved LOD values are lower than the regulatory limits for the respective compounds.

The custom configuration of the TSQ Series triple stage quadrupole mass spectrometer is well-suited for installation in mobile laboratories (Figure 11). Such configuration demonstrates, in addition to the reliability and ruggedness of the TSQ instrumentation, applicability of the system to on-site environmental analysis. In emergency situations, like fires or chemical spills, these mobile facilities are essential for real-time ambient air analysis.

Figure 11: The mobile laboratory of MDDEP Québec, Canada, containing the rugged and reliable TSQ Series triple quadrupole system functioning dynamically on-board.

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