Measurement of Hydrofluorocarbons, Perfluorocarbons and Chlorofluorocarbons in Ambient Air by Gas Chromatography and Mass Spectrometry

Randall Bramston-Cook and Edward Bramston-Cook
Lotus Consulting
5781 Campo Walk
Long Beach, California 90803

Presented at
2014 Air and Waste Management Association 107th Annual Conference
Long Beach, California
June 24-27, 2014

INTRODUCTION

In 1989, the international treaty from the Montreal Protocol on Substances that Deplete the Ozone Layer went into effect and successfully banned most chlorofluorocarbons and other related halocarbons. Hydrofluorocarbons have replaced many of the prohibited chlorofluorocarbons in coolant applications, as they are not regulated under the Montreal agreement. However, they have a major impact on global warming with an estimated 3,830 times more potency than CO_2 and have typical lifetimes of 14 years in the atmosphere, with some significantly longer. The Kyoto Protocol of 1997 set internationally binding emission reduction targets for greenhouse gases not included in the earlier protocol. The Doha Amendment to the Kyoto Protocol in 2012 revised the list of greenhouse gases to be reported as carbon dioxide, methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons, chlorofluorocarbons, sulfur hexafluoride and nitrogen trifluoride.

In September 2013, the US and China had agreed to phase down use of these compounds.[1] Regular monitoring of ambient levels is required to ensure that these elements in global warming continue a downward trend in ambient air levels.

All of these new target gases are measureable by gas chromatography with several detectors. Methane requires a flame ionization detector and carbon dioxide is effectively measured with the same detector with a reduction catalyst. Nitrous oxide and sulfur hexafluoride need an electron capture detector at the levels required for atmospheric measurements.[2,3,4,5] Ambient concentrations of hydrofluorocarbons, perfluorocarbons and chlorofluorocarbons are well below direct detection by mass spectrometry and require cryogenic concentration of a larger sample volume to get the levels mandated. Atmospheric level for nitrogen trifluoride in 2011 was reported at 0.60 pmol/mol (pptV)[6] and is well below reportable levels by mass spectrometry, even with large sample volumes concentrated by cryotrapping. A better detector is likely to be electron capture detector; it is not included in this report.

An often referenced method for measuring hydrofluorocarbons, perfluorocarbons and chlorofluorocarbons is EPA TO-15 Determination of Volatile Organic Compounds in Air.[7] This protocol's listings for chlorofluorocarbons are limited to trichlorofluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane, and 1,2-dichloro-1,1,2,2-tetrafluoroethane, and do not include any hydrofluorocarbons or perfluorocarbons. An alternate method is required to properly report concentrations for these target greenhouse gases.

Table I. Target greenhouse gases and other detectable gases.

Analyte	ASHRAE Number*	CAS Number	Boiling Point (°C)	Global Average Concentration (nmol/mol) as of 2011[6]
Carbon Dioxide	R-744	124-38-9	-78.5 (subl.)	390,500
Methane	R-50	74-82-8	-182.5	1,803
Nitrous Oxide	R-744a	10024-97-2	-88.5	324.2
Nitrogen Trifluoride	--	7783-54-2	-129.1	0.00060
Krypton	R-784	7439-90-9	-153.4	~1,000
Xenon	--	7440-63-3	-108.1	87,000
Sulfur Hexafluoride	--	2551-62-4	-64	0.0073
Tetrafluoromethane	R-14	75-73-0	-127.8	0.079
Hexafluoroethane	R-116	76-16-3	-108.8	0.004
Trifluoromethane	R-23	75-46-7	-82.1	0.024
Pentafluoroethane	R-125	354-33-6	-48.5	0.0096
Difluoromethane	R-32	75-10-5	-52	0.005
1,1,1-Trifluoroethane	R-143a	420-46-2	-47.6	0.012
Octafluoropropane	R-218	76-19-7	-36.7	
Chlorotrifluoromethane	R-13	75-72-9	-81.5	
Dichlorodifluoromethane	R-12	75-71-8	-29.8	0.528
Chlorodifluoromethane	R-22	75-45-6	-40.7	0.213
1,1,1,2-Tetrafluoroethane	R134a	811-97-2	-26.3	0.063
Chloromethane	R-40	74-87-3	-23.8	
Butane	R-600	106-97-8	-1	
Chloroethene	R-1140	75-01-4	-13.4	
1,1,2,2-Tetrafluoroethane	R-134	359-35-3	-19.7	
1,1-Difluoroethane	R-152a	75-37-6	-25	0.0064
1,2-Dichloro-1,1,2,2-tetrafluoroethane	R-114	76-14-2	+3.8	
1-Chloro-1,1-difluoroethane	R-142b	75-68-3	-10	0.021
Dichlorofluoromethane	R-21	75-43-4	+9	
Trichlorofluoromethane	R-11	75-69-4	+23.8	0.238
Chloroethane	R-160	75-00-3	+12.3	
2,2-Dichloro-1,1,1-trifluoroethane	R-123	306-83-2	+27.6	
Dichloromethane	R-30	75-09-2	+39.6	
1,1,2-Trichloro-1,2,2-trifluoroethane	R-113	76-13-1	+47.7	0.074
1,1-Dichloro-1-fluoroethane	R-141b	1717-00-6	+32	0.021
1,1,1-Trichloroethane	R-140a	71-55-6	+74	0.0063
Carbon Tetrachloride	R-10	56-23-5	+76.7	0.086

*American Society of Heating, Refrigerating and Air Conditioning Engineers.

EXPERIMENTAL

Chromatographic Conditions for Hydrofluorocarbons, Perfluorocarbons and Chlorofluorocarbons Measurements

Instrument: Bruker SCION SQ Prime Mass Spectrometer and Bruker 456 Gas Chromatograph

Concentrator Parameters

Trap Cryogen:	Liquid nitrogen
Adsorbent Trap:	multi-layer hydrophobic mixed bed
Initial Temperature:	-48 ^{o}C, hold 14.03 minutes
Temperature Ramp:	+200 ^{o}C/min
Temperature:	+202^{o}C, hold 26.92 minutes
Temperature Ramp	-200 ^{o}C/min
Temperature:	+140^{o}C, hold 6.85 minutes
Cryofocus Trap	90 µl empty trapping
Initial Temperature	+140 ^{o}C, hold 5.00 minutes
Temperature Ramp	-200 ^{o}C/min
Temperature	-195 ^{o}C, hold 9.63 minutes
Temperature Ramp	+200 ^{o}C/min
Temperature	+202 ^{o}C, hold 20.00 minutes
Temperature Ramp:	-200 ^{o}C/min
Temperature:	+140 ^{o}C, hold 11.92 minutes
Mass Flow Controller setting:	50 ml/min
Sample Volume:	500 ml
Sample Processing Interval:	0.01 to 16.40 minutes

Nafion dryer was installed to remove moisture prior to trapping. 150 µL of water was added to all evacuated canisters to generate a final relative humidity level inside of about 50%, to preserve target analytes. On-column injection occurred at 16.40 minutes.

Column Conditions

Column:	J&W GS-GASPRO 60M, 0.32mm, (Agilent, Santa Clara, CA)
Column Flow:	1.5 ml/min with EFC Type 23
Column Oven Cryogen:	Liquid nitrogen
Column Temperature Program:	
Initial Temperature:	+50 ^{o}C, hold 5.00 minutes
Temperature Ramp:	-100 ^{o}C/min
Temperature:	-40 ^{o}C, hold 19.80 minutes
Temperature Ramp:	+100 ^{o}C/min
Temperature:	+10 ^{o}C, hold 2.20 minutes
Temperature Ramp:	+10 ^{o}C/min
Final Temperature:	+110 ^{o}C, hold 5.50 minutes
Temperature Ramp:	+100 ^{o}C/min
Final Temperature:	+240 ^{o}C, hold 0.90 minutes

Mass Spectrometer Parameters

Scan Range for Full Scan: 45 to 300 m/z
Mode: Single Quadrupole
Source: Electron ionization (EI)
Filament Emission Current: 80 µA
Electron Energy: -70 eV
Source Temperature: 200 ^{o}C
Transfer Line Temperature: 150 ^{o}C
Ion Source: 150 ^{o}C
Manifold Temperature: 40 ^{o}C

Full Scan was used for peak locating and Selected Ions Monitoring used for reporting concentrations. Extended Dynamic Range (EDR) was activated. Compound searches were conducted with NIST 11 Spectral Library.

Standards were prepared in 6 liter Summa canister that had been evacuated to below 10 mTorr with Lotus Consulting CC-1 Canister Cleaner, and then humidified with 150 µL purified liquid water prior to loading. Working standards were made from stock gases, from NIST or traceable to NIST, by serial dilutions with Lotus Consulting PS-1 Pressure Station. Multi-level calibrations were performed by varying the sample loading time with a fixed flow rate into the first absorbent trap into a mass flow controller.[9]

RESULTS AND DISCUSSION

Table II lists the number of halogenates labeled as refrigerants, with most responsive to an electron capture detector (ECD).[10] Some of these analytes are extremely sensitive to measurements with electron capture detection. However, this detector generates responses to different compounds that are dramatically variable, with performance based roughly on the number of halogens in the target analyte, with each addition enhancing the signal by roughly an order of magnitude. For example, chloromethane gives a very poor signal, compared with an equal concentration of carbon tetrachloride. Sulfur hexafluoride, at ~7 pmol/mol (pptV), generates a good ECD signal with direct injection without trapping.[5] In addition, with the possibility of ambient samples possessing many of the possible halogenates, coelution is common and the electron capture detector is unable to positively identify closely eluting components, especially when one nearby has an overwhelming signal.

Mass spectrometry allows a positive identification of compounds based on their unique spectral pattern. However, its normal performance with direct injection is expected to range into the low nmol/mol (ppbV) level, and is not sufficient to assay ambient levels of nearly all of the target gases. To allow the spectrometer to measure these low levels well above their detection limits for an accurate assessment of concentrations, large sample volumes were processed through a concentration process to effectively reduce an initial sample volume of 500 ml down to ~ 90 µl for injection into a narrow bore column. The first trap was made up of a multiple layer hydrophobic adsorbent bed designed to ensnare all of the halocarbons, but allow oxygen, methane and carbon

Table II. Number of Halogenates Labeled as Refrigerants.

Type	Number of chemicals given an "R" assignment
Hydroflurocarbon	86
Perfluorocarbon	10
Hydrochlorofluorocarbon	165
Chlorofluorocarbon	22
Hydrochlorocarbon	14
Perchlorocarbon	2

dioxide to pass on through. Effective trapping of tetrafluoromethane mandates that this trap be cooled to -48 ^{o}C. Water in standards and samples would be trapped out as well and could have plugged up this trap. A Nafion dryer was installed prior to the trap to extract water vapor prior to trapping. After loading, the trap contents were heated and transferred to a second cryo-focus trap of narrow tubing with an effective volume of 90 µl. Then this trap was isolated and heated, and then released for direct injection into the separation column. Chromatography started at this point.

Extended Dynamic Range option was activated in the setup for the Bruker SCION mass spectrometer. This option sensed the level of the ion signal every scan and then adjusted the detector voltage and the perceived gain in order to keep the signal output at the optimum level for detection. This dramatically improved the performance for low level analytes, while still allowing larger peaks to be within range. Responses for several of the very low concentration analytes were enhanced by selecting several quantifier ions to be combined together to define the area counts.

A special low-volume sample pressure regulator was installed in the incoming sample line to throttle higher pressures in sample/standard canisters to the same effective pressure and was set to +4 psiG. This process makes the volume allocation into the system independent of sample pressure.[8]

Internal standards were not used with these measurements. Applicable criteria for an internal standard are:

- must not be present in samples,
- must be pure, especially without target analytes,
- must be chemically and physically similar to related analytes, and
- must be chromatographically separated from all targets.

Virtually all combinations of hydrogen, fluorine and chlorine are already deployed in target halogenates (Table II). The first internal standard listed in Method TO-15 is bromochloromethane, which typically elutes well after all of the targets and offers no help in monitoring trapping efficiencies of the earlier-eluting halogenates. The long-term stability of this spectrometer far exceeds any correction available with internal standards.[9,11]

Twenty-nine hydrofluorocarbons, perfluorocarbons and chlorofluorocarbons were either fully separated or distinguishable by their mass spectrum ions, under conditions provided in the experimental section above. Physical properties of these Freons are listed in Table I, and their elution order is listed in Table III and illustrated in Figure 1. Additional analytes are also shown for their associations to elutions of the target gases. Fortuitously, these target analyte have unique spectral ions to make them readily distinguishable from others and also from possible other trace components in air samples.

Table III. Typical retention times and target ions for halogenates.

Analyte	**Typical Retention Time (minutes)**[*]	**Qualifier Ion(s)** [**]	**Quantifier Ion(s)**
Krypton	21.80	**84**, 86	84
Tetrafluoromethane	23.90	50, **69**	69
Xenon	28.56	129, 131, **132**	132
Hexafluoroethane	32.57	50, **69**, 119	69, 119
Sulfur Hexafluoride	32.93	89, 108, **127**	89, 127
Trifluoromethane	33.89	50, 51, **69**	51, 69
Pentafluoroethane	34.02	**51**, 69, 101	51, 101
Difluoromethane	37.02	**51**, 52	51
1,1,1-Trifluoroethane	+	65, **69**	65, 69
Octafluoropropane	37.21	**69**, 100, 119, 169	69, 169
Chlorotrifluoromethane	38.92	50, **69**, 85	69
Dichlorodifluoromethane	38.96	50, **85**, 87, 101	87[***]
Chlorodifluoromethane	39.30	**51**, 67	51
1,1,1,2-Tetrafluoroethane	41.25	51, 63, **69**, 83	69, 83
Chloromethane	41.50	**50**, 52	50, 52
Butane	41.77	**43**, 58	43
Chloroethene	42.37	**62**, 64	62, 64
1,1,2,2-Tetrafluoroethane	+	**51**, 83	51, 83
1,1-Difluoroethane	43.40	47, **51**, 65	51, 65
1,2-Dichloro-1,1,2,2-tetrafluoroethane	44.46	**85**, 87, 135, 137	85
1-Chloro-1,1-difluoroethane	+	45, **65**, 85	45. 65
Dichlorofluoromethane	+	**67**, 69	67
Trichlorofluoromethane	46.00	**101**, 103	101
Chloroethane	47.62	49, 51, **64**, 66	64, 66
2,2-Dichloro-1,1,1-trifluoroethane	+	**83**, 85, 133	83, 85
Dichloromethane	47.93	**49**, 51, 84, 86	49
1,1,2-Trichloro-1,2,2-trifluoroethane	48.95	85, **101**, 103, 151, 153	101, 103, 151
1,1-Dichloro-1-fluoroethane	+	45, 61, **81**, 101	45, 61, 81
1,1,1-Trichloroethane	+	61, **97**, 99, 117, 119	61, 97, 99
Carbon Tetrachloride	+	82, 84, **117**, 119, 121	117, 119, 121

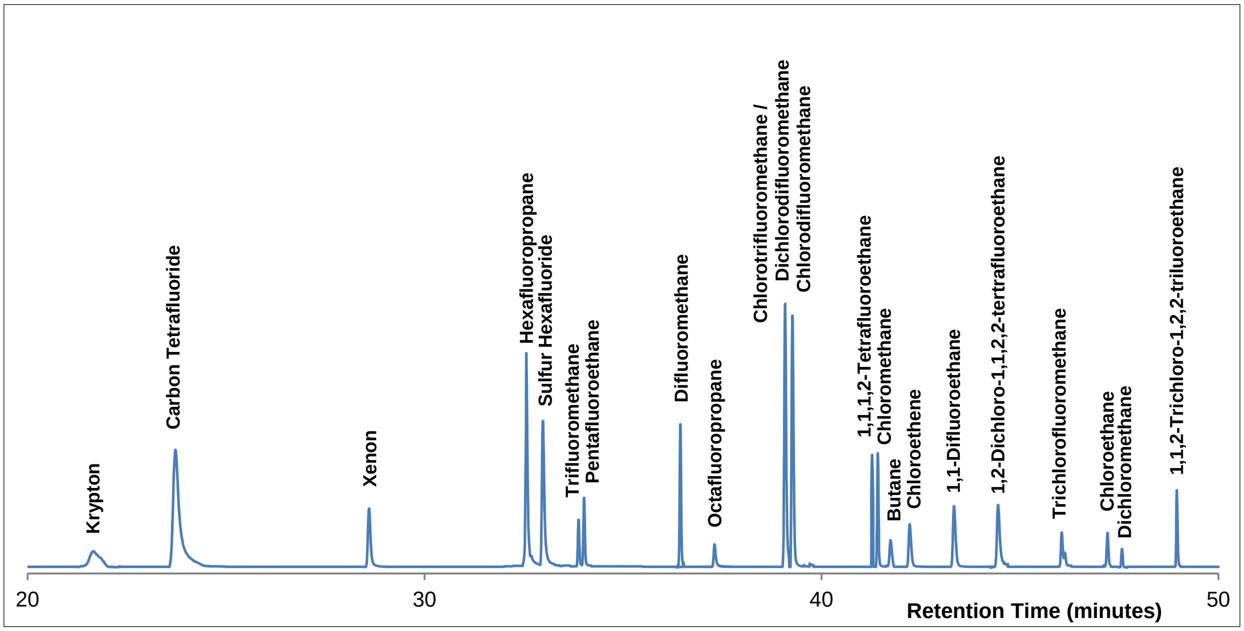
+ Peak locations have not been confirmed, but are listed in their expected elution order.

[*] Sample was injected into the column at 16.40 minutes. The earlier interval involved loading, flushing and transfers of the sample among traps.

[**] Base peaks (largest peak in the mass spectrum) are identified with mass assignments in **bold**.

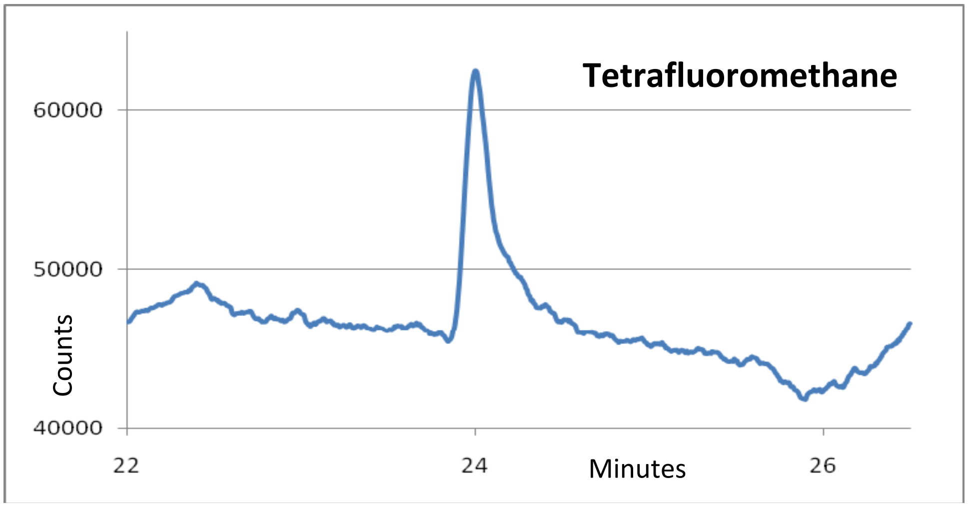
[***] Base ion of 85 cannot be used for quantitation as dichlorodifluoromethane coelutes with chlorotrifluoromethane with the same 85 m/z. Qualifier ions will distinguish the two.

Figure 1. Composite chromatogram of variety of hydrofluorocarbons perfluorocarbons and chlorofluorocarbons, illustrating elution order; confirmed by NIST library searches.



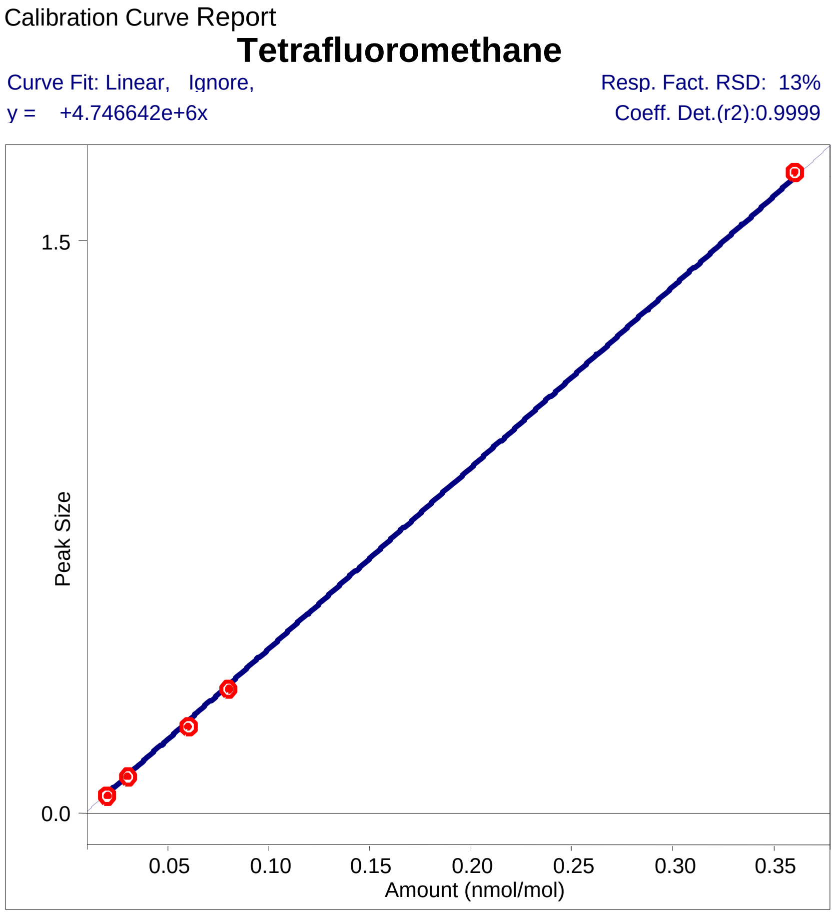
Standards were initially measured with full scan data collection to locate peaks, and these retention times were noted in the workstation compound table. Then the operation was switched to Selected Ions Monitoring (SIM) to enhance detection of the analytes and still maintain confirmation of the peaks by qualifier ions appropriate to the compounds. Figure 2 shows a chromatogram of ambient concentration of tetrafluoromethane. Monitored ions were 69 (quantifier) and 50 m/z. Measured concentration was 71 pmol/mol (pptV). Table III lists the ions selected for qualifiers

Figure 2. Selected ions monitoring chromatogram of tetrafluoromethane in ambient air at Los Alamitos, Ca, on December 11, 2013.



and quantifiers. Signals for some low responders, such as chloromethane, were enhanced by selecting several ions for quantitation. Concentrations were computed from measured area counts through external standard calculations. A representative calibration plot for tetrafluoromethane is shown in Figure 3.

Figure 3. Typical calibration plot for tetrafluoromethane in the pmol/mol range.



Detection limit for tetrafluoromethane was determined from 7 consecutive runs of the lowest standard used in the multi-point calibration (0.010 nmol/mol) and was calculated following protocols given in California Air Resources Board Method 1002.[12] Table IV lists the raw areas for the series and computations to yield a preliminary detection limit of 1.8 pmol/mol (pptV) for tetrafluoromethane. Typical detection limits for this system were in the low single-digit pmol/mol (pptV) range.

Table IV. Computation for limit of detection for tetrafluoromethane.

Area Counts
46,941
52,196
44,381
52,131
49,466
48,329
49,742

$$LOD = \frac{t * s}{m} = \frac{3.0 * 2{,}793}{4{,}746{,}642} = 0.0018\, nmol/mol\, (ppbV)$$

where m = average response factor
t = t-factor for 99% confidence level; 3 for 7 replicates
s = standard deviation of at least five replicates

SUMMARY

Since measurements at concentrations near detection levels are subject to some uncertainties, measurement conditions for ambient levels target halogenates were enhanced as much as possible to achieve signals well above their detection limits to provide a good assessment of their concentrations. These actions included:

- Trapping with multi-layer hydrophobic adsorbents at -48 ^{o}C to effectively snare tetrafluoromethane and others, and allow oxygen, methane and carbon dioxide to pass through to vent,
- Cryofocusing at -195 ^{o}C to sharpen injection of tetrafluoromethane and others into the analytical column,
- Inserting a Nafion dryer to remove sample water prior to injection to avoid trap plugging at the required subzero trap settings and the resulting loss of proper loading of a sample aliquot,
- Activating Extended Dynamic Range to automatically enhance detection of peaks with low responses as well as monitoring ones with major signals,
- Using of Selected Ions Monitoring to both confirm peak identities and calculate concentrations and to dramatically lower measurement noise by eliminating nonessential mass ions,
- Choosing several quantifier ions combined to enhance peak sizes for low concentration analytes, as long as added signal noise does not degrade peak area assignments,
- And installing an in-line sample pressure regulator to properly load standards from pressurized vessels for direct comparison with samples at different pressures, such as real-time sampling of ambient air at atmospheric pressure.

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