DVLS Automatic Air Monitoring Analyser (A^{2}MA)

Provides *in situ* Analysis of VOCs in Urban Air

An instrument has been developed for the automated *in situ* determination of airborne volatile organic compounds (VOCs) using programmed temperature vaporisation injection from a sorbent tube trap. A sorbent tube placed as an injection port liner can be repeatedly used to collect samples of air, with the trapped analytes being subsequently desorbed onto a capillary gas chromatography (GC) column without use of intermediate cryogenic refocussing.

Application Note

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Introduction

Measurements of atmospheric concentrations of volatile organic compounds are currently required in both urban and rural environments, where their presence can be directly detrimental to health, and their ability to form photochemical oxidants in the presence of (NOx) and sunlight is important.

It has also been demonstrated that some hydrocarbons may contribute to global warming and stratospheric ozone depletion and may also accumulate as persistent organic pollutants in some environments. Urban concentrations of VOCs are influenced directly by the emissions from major anthropogenic sources such as vehicle emissions, solvent and petrochemical evaporative losses, gas leaks and many other forms of emission. Many methods for analysing airborne VOCs have been proposed, typically using sorbent traps or evacuated canisters.

Boosting laboratory efficiency

Figure One: In situ VOC analysis in a mobile lab

Carbon molecular sieves of differing mesh sizes are particularly effective in trapping VOCs in air and are frequently incorporated into packed sorbent tubes. Analysis is usually then performed by thermally desorbing the collected sample in a stream of helium over a period of several minutes onto a cryogenically cooled intermediate trap.

The sample is refocussed at the intermediate trap prior to subsequent flash heating, thus introducing the collected analytes as a narrow band onto the analytical column.

A method based on a thermally desorbed adsorption trap and cryo refocussing with liquid nitrogen (LN_2) or carbon dioxide (CO_2) uses typically 50 litres of coolant per day. Whilst methods involving the cryogenic refocussing of sample produce effective analytical separations, the equipment required is both complex and expensive, and the unit requires regular user attention to replenish cryogen supplies.

Placing a sorbent tube as an injection port liner inside a programmed temperature vaporisation (PTV) injector allows rapid desorption of analytes directly into an analytical column. Using this method the traditional intermediate refocussing between desorption and separation is no longer required.

In this technical note we describe the use of on-line sorbent tube sample collection, with programmed temperature vaporisation (PTV) injector for the in situ analysis of ambient air samples.

Experimental

The automation of sample collection and the elimination of the intermediate refocussing step, reduces much of the necessary on-site maintenance required for continuous monitoring, and allows in situ analysis in locations where previously this was not possible.

Using a multi positioning valve, the system can select between standards from, e.g., a tedlar bag or taking sample directly from the outside via, e.g., a probe on the roof of a mobile lab.

Via a smart flow system, sample is pumped through the injector port liner containing a suitable trapping material in reverse flow from bottom to top trapping the analytes, while the carrier gas is re-routed to the GC capillary column by-passing the injector port.

Sampling is during a fixed time with a constant flow controlled with a mass flow controller, without the use of additional coolant as LN_2 or CO_2.

Once the sampling period has finished, the carrier gas via the injector port is re-established. Following, the injection port is heated to desorb the analytes from the injection port liner for transfer to the GC capillary column. In parallel to start heating the injection port liner, the GC–MS analysis has started.

Figure Two: Automatic Air Monitoring Analyzer

Results

The following tables and Figure Three Three show the GC-MS analysis results of a 73-compound standard by the Automatic Air Monitoring Analyzer.

Compound Name	t_R(min)	%RSD	IDL (μg/m³)
Monovinylchloride	6.74	3.48	0.81
Dichlormethane	9.54	2.22	1.37
Trichlormethane	11.81	2.38	1.73
Tetrachlormethane	13.09	3.27	2.59
1,1-Dichlorethane	11.37	2.23	1.28
1,2-Dichlorethane	12.33	2.18	1.26
1,1,1-Trichlorethane	12.99	1.88	1.20
1,1,2-Trichlorethane	14.52	2.40	1.64
1,1-Dichlorethene	9.95	2.02	1.19
cis-1,2-Dichlorethene	11.29	2.17	1.30
trans-1,2-Dichlorethene	10.61	2.02	2.37
Trichlorethene	13.11	2.53	1.77
Tetrachlorethene	14.95	2.50	2.01
1,1-Dichloropropane	13.49	2.38	1.32
1,2-Dichloropropane	13.78	2.51	1.40
1,3-Dichloropropane	14.67	2.59	1.46
Tribromomethane	16.30	2.51	3.37
Chlorobenzene	15.77	2.39	1.18
1,2-Dichlorobenzene	18.17	2.23	1.04
1,3-Dichlorobenzene	17.87	2.55	1.23
1,4-Dichlorobenzene	17.98	2.51	0.91
1,2,4-Trichlorobenzene	20.34	3.54	1.33
Benzene	12.93	2.29	1.03
Toluene	14.86	2.58	1.29
Ethylbenzene	16.53	2.46	1.07
1,2-Dimethylbenzene	16.81	2.56	1.12
1,3&1,4-Dimethylbenzene	16.55	28.04	30.66
Naphthalene	21.22	2.52	0.63
1,2,4-Trimethylbenzene	18.22	2.68	1.17
1,3,5-Trimethylbenzene	17.96	2.33	1.04
i-Propylbenzene	17.65	2.54	1.08
n-Propylbenzene	17.95	2.77	1.18
Styrene	16.75	2.50	1.07
a-Methylstyrene	17.97	3.09	1.15
Indane	18.46	14.07	6.67
Decaline	20.13	2.01	0.92
MTBE	12.36	3.19	1.90
ETBE	13.59	3.98	2.36
Diethyl ether	10.63	2.07	1.18
n-Propane	5.46	6.12	5.42
n-Butane	8.51	2.14	4.20

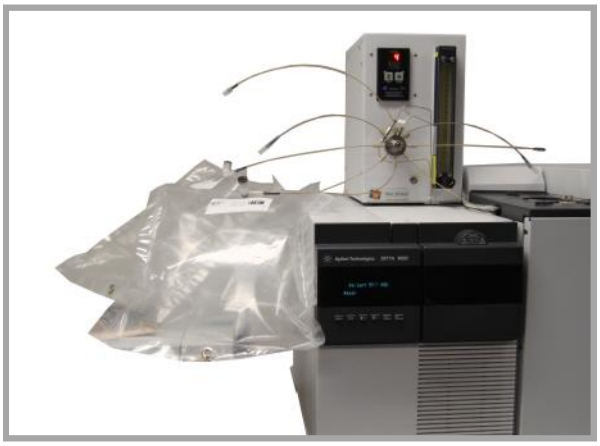
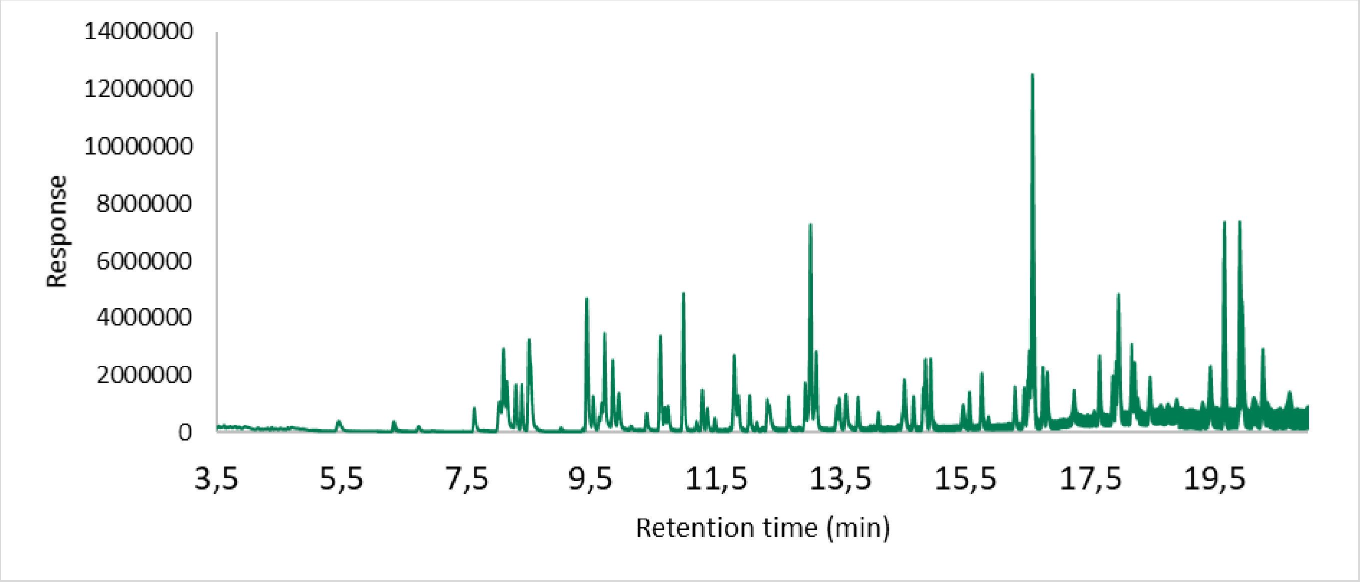


Table Two: Continued GC-MS analysis results of a 73-compound standard

Compound Name	t_R(min)	%RSD	IDL (μg/m^3)
n-Pentane	10.98	2.02	3.50
n-Hexane	13.02	2.66	5.20
n-Heptane	14.83	3.47	1.20
n-Octane	16.50	3.37	1.22
n-Nonane	17.91	3.03	1.13
n-Decane	19.43	5.18	2.67
n-Undecane	21.60	33.97	21.96
i-Butane	8.04	1.81	1.52
Methylcyclopentane	13.01	2.15	0.80
Cyclohexane	13.44	2.25	0.85
4-vinyl-1-Cyclohexene	16.44	5.51	2.19
1,3-Butadiene	8.10	2.14	1.59
Isoprene	10.74	1.95	0.65
1-Butyne	8.30	2.48	1.89
Methanol	4.71	3.29	2.94
Ethanol	7.64	2.53	2.24
1-Propanol	10.39	2.44	1.39
2-Propanol	9.67	5.77	4.17
1-Butanol	12.66	3.22	2.17
2-Butanol	12.04	3.30	2.10
Propanone	9.44	1.69	1.27
Butanone	11.80	2.20	1.84
Cyclohexanone	16.55	2.78	2.03
2,3-Butadion	11.73	2.85	3.98
Tetrahydrofuran	11.86	1.74	1.21
Benzaldehyde	17.25	3.05	1.45
Acrylonitrile	9.63	2.29	0.69
Carbonyl sulfide	3.97	12.42	18.70
Methylmercaptane	6.96	14.04	13.58
Methyl disulfide	9.72	2.09	3.15
Dimethyl sulfide	9.85	2.39	2.63

Figure Three: Total-ion-current GC–MS chromatogram of a 73-compound standard



Using this system, VOC in air can be monitored with a relative standard deviation (%RSD, 8 runs at 8 - 70 µg/m3) of typically 1 - 5 % and an Instrument Detection Limit (IDL) in the range of 0.5 - 6 µg/m3.

Conclusions

The DVLS Automatic Air Monitoring Analyzer (A^{2}MA) has been demonstrated.
Air samples are automatically enriched on a sorbent tube in a GC injection port and subsequently analyzed by GC–MS.
The system is proven for the *in situ* analysis of VOCs in airborne samples in a mobile lab for a wide variety of potential air polluting compounds without the use of LN_2 or CO_2 as trapping coolant. % RSD is in the range of typically 1 – 5 % and ILD in the range of 0.5 – 6 µg/m3.

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