

# Analysis of Environmental Samples with a Novel Atmospheric Pressure GC Source Coupled to High-Resolution TOF-MS Analysis



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## Authors:

T. Arthen-Engeland<sup>1</sup>, A. Steiler<sup>1</sup>, A. Holle<sup>1</sup>, P. Decker<sup>1</sup>, J. Anacleto<sup>1</sup>, C. Baessmann<sup>1</sup>  
<sup>1</sup>Bruker Daltonik GmbH, Bremen, Germany

## Overview:

A new GC-APCI source coupled to a high-resolution Q-TOF-MS was used for the GC/MS analysis of PAH, pesticide and explosive standards and of soil, sediment and sludge samples of environmental origin. Compared to an earlier GC-APCI design we observed improved GC/MS performance regarding reproducibility and analytical working range.

## Introduction:

While electron ionization GC/MS has been used for more than 40 years in environmental analytical chemistry, the use of GC-APCI-MS has gained more interest in the last several years [1-3]. GC-APCI is a flexible atmospheric pressure chemical ionization source that can produce lower detection limits than electron ionization and in combination with high-resolution MS enables the identification of unknown analytes: The soft APCI ionization preserves the molecular ion information and allows the identification of trace contaminations or degradation products which could not yet be identified due to missing library data or missing standards.

In the present study we used a new GC-APCI II source. The source consists of an APCI source chamber equipped with a corona discharge needle assembly and a flexible heated GC transfer line. While other GC-APCI sources use a fixed GC-transfer line design the GC-APCI II source allows easier handling of the GC and a quicker exchange of the chromatography type, e.g. from GC to LC source and GC to LC chromatographic system (and vice versa). Compared to earlier designs the GC-APCI II source was further developed in the following respect:

- The whole source was designed much tighter to exclude uncontrolled gas exchange with the outside air and to control the water content in the ion source.
- The APCI vaporizer heater used in the previous design is omitted within the GC-APCI II ion source, thus suppressing gas turbulences due to a high vaporizer gas flow.
- The heat required for the APCI process is generated in close vicinity to the ionization region and is preserved there by shielding the ionization region from the outer source area.
- All gas flows within the ion source were optimized to reduce turbulences and to guide the GC eluent flow into the ion source.

Finally this source supports also a mass calibration module which allows automatic MS calibration by injecting PFTBA calibration gas into the ion source chamber during each GC/MS run.

Fig. 1: Scheme of the GC-APCI II ion source.

The GC-effluent is directed from the GC transfer line (left) into the APCI region of the ion source. Mechanical design, gas flows, heat distribution and electrical fields are optimized for efficient AP chemical ionization and ion transfer into the MS inlet. The GC-APCI II source is equipped with an automatic calibration gas module that flushes calibration gas into the APCI region.

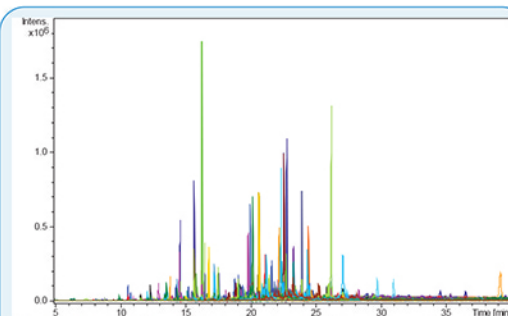
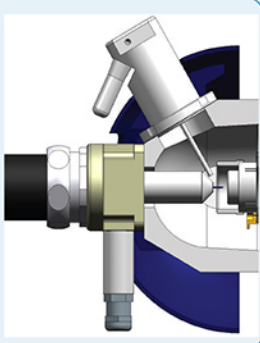


Fig. 2: EICs of PAHs and alkyl-substituted PAHs in the extract of a sediment sample (#534537); conc. are in the 100 pg/µl range.

## Methods:

Standard solutions of polycyclic aromatic hydrocarbons (PAH Calibration Mix, Sigma No. 4-7940-U), of a pesticides mixture containing 60 pesticides [5] and of explosives (Combined Stock Solution, Ultra Scientific No. NAIM-833E) were diluted in dichloromethane to appropriate concentrations for the generation of calibration curves between 0.5 and 500 pg/µl, respectively 1 ng/µl for the explosives. Soil samples were extracted in quick solid-liquid extraction procedures using acetone and sonication. Sediment samples were used as provided. The sludge sample was extracted in methanol, centrifugated and diluted in dichloromethane. For all analyses one µl of each sample was injected into the GC.

GC/MS analysis was performed using a Bruker 450-GC with PAL Combi-xt Autoinjector and a impact Q-TOF mass spectrometer or an impact HD Q-TOF-MS (both Bruker Daltonics). The GC was operated with a 30 m BR-5ms FS capillary column (0.25 mm ID, 0.25 µm film thickness), operated at 1 ml/min constant helium flow and a GC oven temperature program at 50°C (1 min) - 10°C/min - 290°C (5 or 15 min). Splitless injection was at 250°C. Data were acquired from 50 - 1000 m/z at 6 spectra per second, operated in the positive and in the negative ionization mode. Spectra were externally calibrated using PFTBA as calibration gas injected automatically into the APCI source at the beginning of each MS run. DataAnalysis and TargetAnalysis software (Bruker Daltonics) was applied for peak detection and data evaluation.

## Results:

The idea of this feasibility study was to test the applicability of the new GC-APCI II source with different classes of environmental target compounds in positive and in negative ionization mode. We therefore selected PAHs as unpolar and pesticides and explosives as polar chemical compounds to demonstrate the broad applicability. Before the analyses of some selected samples we analyzed a series of calibration standards with N=3 replicates.

In previous applications we had tested various pesticides (> 800) with LC/ high-resolution Q-TOF-MS where we selected a representative mixture of 60 pesticides of high relevance for analytical monitoring [e.g. 5]. In this study we found 40 of the 60 components to be easily analyzable by GC-APCI II/TOF-MS in positive ionization and selected 15 of them for substance calibration in the concentration range of 1 - 500 pg/µl each. Fig. 3 shows typical extracted chromatograms (Δ EIC = 5 mDa) and the analytical parameters for the quantified pesticides are shown in Table 1. The components are eluting in very sharp and highly reproducible GC peaks. There is hardly any variation in retention time and peak width, while area RSD in most cases is 5 %. There are 2-3 poorer area reproducibilities, e.g. we found Thiocloprid with a broad, tailing GC peak signal and systematic decrease. We will have a closer look at those few components in future studies. A sludge sample was quantified for Pyrimethanil (0.4 ng/µl), Myclobutanil (0.7 ng/µl), Pirimicarb (0.5 ng/µl).

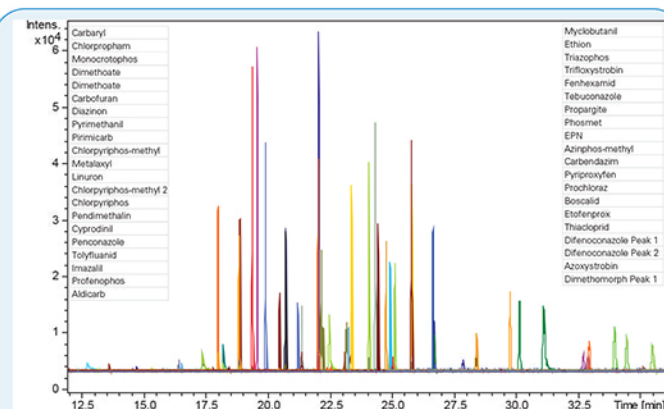


Fig. 3: GC/MS run of a pesticide LC/MS test mix, 50 pg/µl each [5]. 40 of 60 pesticides were found by GC/MS; substances are listed in order of elution. (Δ EIC = 5 mDa)

Additionally, 16 PAHs were calibrated in the positive ionization mode and we found LLOQs (lower limits of quantification) in the low pg/µl range. Analytical results are consistent to another recent GC-APCI II study where we used a Restek Rxi-PAH capillary column with superior GC-separation and therefore found better S/N values and a factor of ca. f=10 lower LLOQs for the PAHs [unpublished results]. The calibration was used to quantify PAHs in the liquid extract of some sediment samples containing a complex mixture of PAHs and alkyl-chain substituted PAHs (Fig.2).

Finally, GC-APCI/MS was applied for the quantification of aromatic explosives. Most of these compounds are preferably analyzed in the negative ionization mode but due to the inherent instability of this compound class mass spectra are very complex with a lot of fragmentation in negative APCI. The calibration in the concentration range of 1 to 1000 pg/µl was applied to the quantification of a soil sample from a former WW II explosive production plant identifying several production by-products and (microbiological) degradation products (Fig.4).

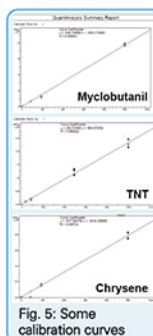


Fig. 5: Some calibration curves

PAH	RT [min]	FWHM [s]	Area %	S/N	LLOQ [pg/µl]	R <sup>2</sup>	Calc. Mass [M+H] <sup>+</sup> [Da]	Exper. Mass [M+H] <sup>+</sup> [Da]	Stand. Dev. SD [mDa]	Rel. SD RSD [ppm]	Mass Dev. [mDa]	Mass Dev. [ppm]
Acenaphthene	16.34	2.2	1.3	453	n/c	n/c	155.08553	155.08597	0.010	0.62	0.45	2.88
Fluorene	17.54	2.2	1.9	718	2	0.9997	167.08553	167.08561	0.006	0.37	0.09	0.52
Phenanthrene	19.79	2.2	2.2	559	1	0.9998	179.08553	179.08535	0.002	0.12	0.17	0.99
Anthracene	19.93	2.2	1.9	279	5	0.9994	179.08553	179.08533	0.002	0.22	0.20	1.10
Fluoranthene	22.51	2.2	2.7	1040	1	0.9997	203.08553	203.08519	0.004	0.18	0.33	1.64
Pyrene	23.14	2.3	3.2	939	5	0.9989	203.08553	203.08513	0.002	0.08	0.40	1.97
Benzo[a]anthracene	26.06	2.5	4.5	604	6	0.9982	229.10118	229.10035	0.009	0.38	0.83	3.61
Chrysenes	26.16	2.5	3.8	628	2	0.9997	229.10118	229.10041	0.003	0.13	0.76	3.33
Benzo[b]fluoranthene	29.56	2.6	4.5	264	8	0.9965	253.10118	253.10067	0.010	0.40	0.51	2.00
Benzo[k]fluoranthene	29.67	2.6	4.7	249	18	0.9832	253.10118	253.10066	0.011	0.44	0.56	2.21
Benzo[a]pyrene	30.93	4.2	5.1	168	20	0.9844	253.10118	253.10075	0.008	0.30	0.42	1.67
Dibenz[ah]anthracene	37.18	6.5	5.0	249	32	0.9889	277.10118	277.10068	0.011	0.41	0.50	1.79
Benzo[ghi]perylene	37.40	6.8	4.8	60	30	0.9918	279.11683	279.11623	0.015	0.53	0.60	2.14
Indeno[1,2,3-cd]pyrene	39.03	7.6	5.5	118	20	0.9979	277.10118	277.10065	0.001	0.04	0.53	1.91
<b>Pesticide</b>												
Chlorpropham	18.04	2.0	1.4	521	2	0.9998	172.015826	172.01624	0.006	0.32	0.25	1.48
Dimethoate	18.89	2.4	2.1	37	6	0.9992	230.066976	230.06629	0.017	0.74	0.60	2.63
Carbofuran	18.93	2.0	2.9	422	4	0.9994	222.112698	222.11231	0.011	0.48	0.16	0.72
Diazinon	19.42	1.8	2.9	2372	2	0.9997	305.108262	305.10841	0.010	0.32	0.08	0.26
Pyrimethanil	19.61	2.0	14.4	1632	3	0.9997	200.1182239	200.11816	0.006	0.31	0.06	0.30
Pirimicarb	19.95	2.0	1.6	1096	4	0.9993	239.1502523	239.14951	0.001	0.05	0.75	3.12
Chlorpyrifos-methyl 1	20.51	1.9	1.9	296	4	0.9996	321.9022599	321.90195	0.006	0.17	0.31	0.95
Chlorpyrifos-methyl 2	21.40	1.8	8.3	68	4	0.9996	321.9022599	321.90202	0.006	0.20	0.24	0.76
Pendimethalin	22.05	1.9	4.9	785	1	0.9999	212.0668822	212.06659	0.012	0.57	0.01	0.04
Myclobutanil	23.39	2.1	2.3	1012	4	0.9996	289.1215507	289.12152	0.014	0.48	0.07	0.25
Fenhexamid	24.93	2.0	20.6	359	6	0.9997	302.0709107	302.07047	0.005	0.15	0.44	1.46
EPN	25.81	2.1	7.0	1240	1	0.9998	324.0453916	324.04560	0.010	0.29	0.21	0.65
Thiocloprid	31.14	6.6	41.5	139	11	0.9952	253.0309212	253.03071	0.005	0.20	0.21	0.82
Azoxystrobin	33.94	4.7	2.1	257	5	0.9996	404.1240971	404.12398	0.009	0.22	0.12	0.30
Dimethomorph	34.42	4.8	0.9	149	5	0.9995	388.1310124	388.13051	0.004	0.11	0.51	1.30
Dimethomorph 2	35.46	5.2	0.6	114	n/c	n/c	388.1310124	388.13039	0.008	0.21	0.62	1.60
<b>Explosives (neg. ionisation)</b>												
Nitrotoluene NT	8.03	1.2	11.5	4	50	0.999	136.04040	136.04050	0.001	4.10	0.10	0.71
Nitrotoluene NT	8.32	1.3	6.3	4	50	0.9993	136.04040	136.04090	0.000	2.70	0.50	3.68
Nitrotoluene NT	8.47	1.3	7.1	7	50	0.9994	136.04040	136.04058	0.000	2.79	0.18	1.32
Dinitrotoluene DNT	10.17	1.5	7.6	8	5	0.9992	167.00983	167.01065	0.001	4.28	0.82	4.89
Dinitrotoluene DNT	10.21	1.8	8.1	27	5	0.9984	181.02548	181.02580	0.001	2.82	0.32	1.79
Dinitrobenzene DNB	10.82	1.8	4.0	23	5	0.9995	181.02548	181.02572	0.001	3.57	0.24	1.33
Trinitrobenzene TNB	12.00	1.8	6.5	60	0	0.9994	213.00273	213.00297	0.001	3.90	0.24	1.14
Trinitrotoluene TNT	12.06	1.8	8.1	30	5	0.9992	227.01838	227.01895	0.001	3.07	0.17	0.76
Amino-Dinitrotoluene A-DNT	14.07	2.0	5.1	30	5	0.9996	196.03638	196.03661	0.001	3.05	0.23	1.19
Amino-Dinitrotoluene A-DNT	14.57	2.1	6.0	37	5	0.9995	196.03638	196.03661	0.001	2.69	0.23	1.17
Tetryl	15.29	1.8	80.2	4	50	0.9999	241.02146	241.02230	0.001	3.36	0.84	3.47

Table 1: Statistical results of N=3 replicate GC/MS runs of PAH, pesticides and explosive standards at 50 pg/µl concentration of each component: retention time, GC peak half-width, relative standard deviation (RSD) of area, average S/N and experimentally determined masses including their standard deviations SD and average mass deviation are shown. Calibration was performed in the analytical range of 0.1 to 500 pg/µl for PAH + pesticides and up to 5 ng/µl for the explosives; lower limits of quantification LLOQ and linearity are listed for each component.

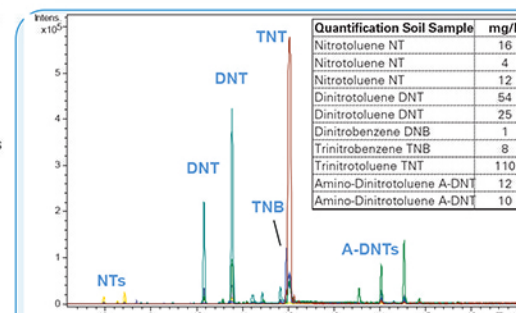


Fig. 4: GC/MS run of a liquid extract of an explosive soil sample: main component is TNT, but also the by-products from the production process as well as degradation products were found.

Quantification Soil Sample	mg/kg
Nitrotoluene NT	16
Nitrotoluene NT	4
Nitrotoluene NT	12
Dinitrotoluene DNT	54
Dinitrotoluene DNT	25
Dinitrobenzene DNB	1
Trinitrobenzene TNB	8
Trinitrotoluene TNT	110
Amino-Dinitrotoluene A-DNT	12
Amino-Dinitrotoluene A-DNT	10

## Conclusions:

Here we reported the application of a novel GC-APCI II ion source for the investigation of standards and samples of environmental origin at impact and an impact HD Q-TOF-MS.

- We demonstrated improved GC-APCI II/TOF-MS performance for the calibration of PAH, pesticide and explosive standards and for the quantification of some environmental samples in the negative and in the positive ionization mode.
- Reproducibility and quantification results are very satisfying: the analytical (linear) working range was about > 2.7 orders of magnitude at linearities better than R<sup>2</sup> > 0.99 for nearly all target compounds
- We observed better lower limits of quantification (LLOQs) for most of the standards due to reduced chemical background in the ion source.
- And finally we observed excellent mass accuracy in the low one-digit ppm range or even below.
- Based on this feasibility study we will extend this work for a broader range of pesticides and for the negative ionization mass spectra of explosives.

## References:

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