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# Possibilities of gas chromatography–atomic emission detection in pesticide multiresidue analysis Application to herbicide analysis in soils

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**Abstract**

The potential of gas chromatography with atomic emission detection (GC–AED) for pesticide multiresidue analysis is explored. Retention data of 181 phytochemicals of diverse properties and considerations about the identification reliability and sensitivity are provided, making a comparison with data obtained by mass spectrometric (MS) detection. The GC–AED system is applied to the determination of 11 herbicides in laboratory-spiked soils after extraction with ethyl acetate. Complementary use of MS is required in order to resolve some peak pairs undiscerned by AED.

*Keywords:* Environmental analysis; Detection, GC; Soil; Pesticides

## 1. Introduction

The necessity of knowing in an environmental sample as many related compounds (e.g. pesticides) as possible has fostered the development of multiresidue analysis protocols, in which special attention must be devoted to the sample preparation and chromatographic determination steps. Conventional solvent extraction and clean-up (liquid–liquid partitioning, gel permeation chromatography, adsorbent packed columns) procedures have been applied to the pesticide analysis from very different families on environmental and foodstuffs samples [1–11]. Solid-phase extraction [12–15] or, more recently, supercritical fluid extraction [16–19] have also been used. The extracted pesticides can be fractionated into several groups, prior to chromatographic analysis in order to simplify their identification in the chromatogram [20–22].

As regards chromatographic determination, gas chromatography (GC) with capillary columns and low-polarity stationary phase is the most used technique on account of its high resolving power and the availability of sensitive and selective detection methods such as the electron-capture (ECD), nitrogen–phosphorus (NPD) and flame photometric detection (FPD). Recent hyphenated techniques resulting from combinations of GC with mass spectrometry (MS), Fourier transform infrared spectroscopy or, lately, atomic emission spectrometry, afford more reliable identification of the compounds, particularly those in extracts from complex samples [23–29].

With atomic emission detection (AED), monitoring characteristic wavelengths for carbon and hydrogen atoms provides universal, non-selective chromatograms, similar to those obtained with flame ionization detection. On the other hand, monitoring

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the emission lines for other elements such as phosphorus, nitrogen and sulphur ensures specific chromatograms for that element, increasing markedly the selectivity, which is specially desirable in dealing with environmental and food samples [30–33].

The growing use of atomic emission as detection technique led us to explore the potential of a GC–AED system for the pesticide multiresidue analysis. So, retention data and complementary information for 181 pesticides and related compounds, including some with polarities or thermal properties inappropriate for GC analysis [34–36], are provided. Sensitivity and linearity data provided by the GC–AED equipment are compared with those obtained by GC–MS. The GC–AED multiresidue system, in conjunction with a GC–MS configuration, is used to screen 11 herbicides in laboratory-spiked soils after extraction with ethyl acetate and clean-up on octadecylsilane (ODS) cartridges and it is also used to monitor the residues in 90 soil samples where cereals are grown.

## 2. Experimental

### 2.1. Standards and reagents

Hexane, methanol and ethyl acetate residues, analysis grade, were purchased from Scharlau (Barcelona, Spain).

Chemicals and pesticide standards were supplied by Chemservice (West Chester, PA, USA), Promochem (Wesel, Germany) and Riedel-de Haën (Seelze, Hannover, Germany). ODS cartridges (500 mg) were obtained from Waters (Milford, MA, USA).

### 2.2. Preparation of spiked soils

A portion of 20 g of soil, previously dried at room temperature and sieved, was treated with 2 ml of methanol containing a known amount of each herbicide. The sample was then homogenized in a mixer for 10 min and subsequently stored at room temperature in the darkness for 2 h, prior to extraction.

The experiments described were conducted with soil of the following composition: 27.3% clay; 52.4% sand; 20.3% silt and 1.8% organic matter.

### 2.3. Extraction and clean-up of herbicides in soils

An amount of 20 g of soil was extracted with two portions of 100 ml of ethyl acetate under mechanical stirring for 30 min, after which the liquid phase was separated from the solid residue by centrifugation at 3500 *g* for 10 min. The two extracts were combined and made to 3 ml in a Zymark evaporator (Hopkington, MA, USA), heating at 30°C under a gentle stream of nitrogen. The solution was percolated through an ODS cartridge (that was previously conditioned by elution of 10 ml of methanol and 10 ml of ethyl acetate) and then, the cartridge was eluted with further 3 ml of ethyl acetate. After that, both eluates were combined and evaporated to dryness. Finally, the dry extract was collected with 3 ml of methanol (concentration factor, 66) and injected into the GC instrument.

### 2.4. Chromatographic equipments

Two Hewlett-Packard (Avondale, PA, USA) 5890 Series II gas chromatographs, directly coupled by a transfer line to an HP5921A atomic emission detector and an HP5989A mass spectrometer, have been used. Both chromatographs were fitted with a 30 m×0.53 mm, 0.50 $\mu$m HP-608 column. GC–AED was performed as follows: helium as carrier gas; pressure programme, initially pressure 8 kPa, 551.6 kPa/min ramp up to 69 kPa (held for 0.7 min), 682.6 kPa/min ramp up to 8 kPa, and finally 1.4 kPa/min ramp up to 141 kPa; temperature programme, initially 50°C (held for 1 min), 3 C°/min ramp up to 275°C (held for 15 min); injection in splitless mode, injected volume 2 $\mu$l; injection and transfer line temperatures, 200 and 280°C, respectively. The AED instrumental settings consisted of: make-up flow 30 ml/min; cavity temperature 280°C; scavenger gas, filter and backamount adjustment set according to Hewlett-Packard default specifications.

The working conditions for the GC–MS system were as follows: helium as carrier gas; pressure programme, initially 3 kPa, 682.6 kPa/min ramp up to 69 kPa (held for 0.55 min), 682.6 kPa/min ramp down to 4 kPa, and finally 1.3 kPa/min ramp up to 119 kPa (held for 3 min); temperature programme, initially 50°C (held for 1 min), 3 C°/min ramp up to 275°C (held for 15 min); injection in splitless mode,

Table 1
Chromatographic characteristics and limits of detection (LOD) of the pesticides analyzed by GC–AED and GC–MS

| Compound | AED-C193 | | MS-SCAN | | | |
|---|---|---|---|---|---|---|
| | Retention time (min) | LOD mg/l | Retention time (min) | LOD mg/l | Peak | GC |
| 1,2-Dichloropropene | 5.35 | 10 | N.D. | N.D. | P | N |
| Thiophanate | 13.73 | 8 | 4.28 | 3 | P+ | N |
| Amitrole | 20.87 | 15 | 12.47 | 6 | P | Y |
| Propoxur | 20.87 | 0.1 | 12.46 | 4 | P | N |
| 2,4-Dichlorophenol | 21.48 | 0.04 | 12.61 | 0.8 | P | Y |
| Carbonalate | 23.27 | 0.2 | 14.15 | 3 | D+ | N |
| Dichlorvos | 25.75 | 0.01 | 17.62 | 0.2 | P | Y |
| EPTC | 27.35 | 0.05 | 19.52 | 1 | P | Y |
| 2,4,5-Trichlorophenol | 27.90 | 0.04 | 20.28 | 0.2 | P | Y |
| Methamidophos | 27.90 | 0.07 | 20.27 | 0.4 | P | Y |
| Butylate | 28.65 | 0.2 | 21.10 | 2 | P | N |
| Propamocarb | 29.19 | 0.4 | 21.60 | 4 | P | N |
| Biphenyl | 29.48 | 0.01 | 22.02 | 1 | P | Y |
| Tribenuron | 29.59 | 0.5 | 22.15 | 5 | D+ | N |
| Dichlobenil | 29.69 | 0.01 | 22.25 | 0.1 | P | Y |
| Vernolate | 30.00 | 0.06 | 22.61 | 0.8 | P | N |
| Pebulate | 30.69 | 0.2 | 23.37 | 2 | P | N |
| Propham | 32.14 | 0.08 | 24.91 | 3 | P | N |
| Phosdrin mevinphos | 32.79 | 0.009 | 26.15 | 0.2 | P | Y |
| Trichlorphon | 33.68 | 0.008 | 26.82 | 0.3 | P | Y |
| Daminozide | 34.50 | 0.03 | 27.60 | 0.5 | D | N |
| Molinate | 35.21 | 0.06 | 28.38 | 0.9 | D | N |
| Acephate | 35.34 | 0.02 | 28.45 | 1 | P | Y |
| Trifluralin | 35.79 | 0.003 | 29.03 | 0.08 | P | Y |
| Dinitre-*o*-cresol | 37.04 | 0.008 | 30.41 | 0.1 | D | Y |
| Cycloate | 37.12 | 0.02 | 30.51 | 0.3 | P | N |
| Oxamyl | 37.40 | 0.07 | 30.82 | 1 | P | N |
| Propachlor | 37.97 | 0.01 | 31.45 | 0.1 | P | Y |
| Chlorpropham | 38.09 | 0.08 | 31.59 | 3 | P | N |
| Ethoprophos | 38.24 | 0.02 | 31.79 | 0.5 | P | Y |
| Phosmet | 38.32 | 0.01 | 31.90 | 0.3 | P | Y |
| TEPP | 38.42 | 0.03 | 31.93 | 0.4 | P | Y |
| HCB | 38.52 | 0.008 | 31.98 | 0.08 | P | Y |
| Chlordimeform | 38.67 | 0.08 | 32.23 | 0.2 | P | Y |
| Fluometuron | 38.69 | 0.1 | 32.35 | 1 | D | N |
| 2,4-D methyl ester | 39.11 | 0.006 | 32.70 | 0.08 | P | Y |
| Diallate | 39.23 | 0.01 | 32.84 | 0.1 | M | Y |
| Cymoxanyl | 39.25 | 0.07 | 32.87 | 2 | D | N |
| Demeton-S-methyl | 39.27 | 0.04 | 33.19 | 0.3 | P | Y |
| Methomyl | 39.81 | 0.07 | 33.49 | 4 | D | N |
| Phorate | 39.97 | 0.009 | 33.77 | 0.2 | P | Y |
| α-HCH | 40.06 | 0.006 | 33.97 | 0.09 | P | Y |
| Trimethacarb | 40.20 | 0.2 | 33.92 | 6 | P+ | N |
| Dibrom | 40.28 | 0.009 | 34.12 | 0.09 | P | Y |
| Phenmediphan | 40.50 | 0.04 | 34.26 | 0.2 | P | N |
| Omethoate | 40.53 | 0.03 | 34.43 | 0.2 | P | Y |
| Fenuron | 40.63 | 0.2 | 34.50 | 2 | D | N |

(Continued on p. 248)

Table 1 (*continued*)

| Compound | AED-C193 | | MS-SCAN | | | |
|---|---|---|---|---|---|---|
| | Retention time (min) | LOD mg/l | Retention time (min) | LOD mg/l | Peak | GC |
| Thiometon | 41.32 | 0.02 | 35.40 | 0.1 | P | Y |
| Pentachlorophenol | 41.43 | 0.01 | 35.35 | 0.1 | P | Y |
| Sulfallate | 41.58 | 0.3 | 35.46 | 4 | D | N |
| Pentachloronitrobenzene | 41.65 | 0.01 | 35.53 | 0.09 | P | Y |
| Terbufos | 41.78 | 0.03 | 35.92 | 0.09 | P | Y |
| Dinoseb | 41.86 | 0.2 | 36.26 | 0.5 | P | N |
| Dicloran | 41.87 | 0.02 | 36.26 | 0.3 | P | Y |
| Diuron | 42.12 | 0.2 | 36.50 | 2 | D+ | N |
| Lindane | 42.43 | 0.005 | 36.90 | 0.08 | P | Y |
| Desmedipham | 42.43 | 0.01 | 36.95 | 0.7 | D | N |
| Triallate | 42.64 | 0.002 | 37.01 | 0.3 | P | Y |
| Propazine | 42.65 | 0.02 | 36.96 | 0.1 | P | Y |
| Atrazine | 42.69 | 0.03 | 37.02 | 0.1 | P | Y |
| Terbuthylazine | 42.82 | 0.02 | 37.01 | 0.2 | P | Y |
| Ethylenethiourea | 42.83 | 0.4 | 37.01 | 3 | P | N |
| Diazinon | 42.87 | 0.01 | 37.19 | 0.1 | P | Y |
| Simazine | 42.93 | 0.03 | 37.34 | 0.1 | P | Y |
| $\beta$-HCH | 43.15 | 0.01 | 37.55 | 0.07 | P | Y |
| Monocrotophos | 43.53 | 0.02 | 38.18 | 0.3 | P | Y |
| Aminocarb | 43.79 | 0.5 | 38.25 | 2 | P+ | N |
| Heptachlor | 44.24 | 0.006 | 38.40 | 0.05 | P | Y |
| Dimethoate | 44.36 | 0.009 | 38.69 | 0.1 | P | Y |
| Chlorsulfuron | 44.57 | 0.3 | 38.77 | 0.1 | D+ | N |
| Carbofuran | 44.75 | 0.2 | 38.97 | 0.8 | P | N |
| $\delta$-HCH | 45.17 | 0.01 | 39.44 | 0.09 | P | Y |
| Vinclozolin | 45.28 | 0.005 | 39.52 | 0.09 | P | Y |
| Terbucarb | 45.47 | 0.5 | 39.77 | 3 | D+ | N |
| Metobromuron | 45.52 | 0.2 | 39.83 | 2 | D | N |
| Chloroxuron | 45.88 | 0.2 | 40.23 | 2 | D+ | N |
| Terbacil | 45.94 | 0.03 | 40.29 | 0.5 | P | Y |
| Aldrin | 45.98 | 0.005 | 40.21 | 0.3 | P | Y |
| Alachlor | 46.12 | 0.007 | 40.49 | 0.1 | P | Y |
| Z-Chlorfenvinphos | 46.45 | 0.008 | 40.86 | 0.06 | P | Y |
| Propanil | 46.48 | 0.04 | 40.89 | 0.3 | P | Y |
| Fenchlorphos | 46.57 | 0.04 | 41.12 | 0.1 | P | Y |
| Pirimicarb | 46.62 | 0.04 | 41.05 | 0.2 | P | Y |
| Chlorpyrifos methyl | 46.68 | 0.001 | 41.13 | 0.1 | P | Y |
| Monuron | 46.79 | 0.3 | 41.24 | 4 | D+ | N |
| Parathion methyl | 47.08 | 0.02 | 41.68 | 0.1 | P | Y |
| Phosphamidon | 47.19 | 0.009 | 41.86 | 0.2 | M | Y |
| Prometryn | 47.24 | 0.008 | 41.89 | 0.1 | P | Y |
| Ametryn | 47.56 | 0.009 | 42.09 | 0.1 | P | Y |
| Metalaxyl | 47.92 | 0.02 | 42.35 | 0.3 | P | Y |
| Linuron | 47.97 | 0.2 | 42.45 | 2 | D | N |
| Pirimiphos methyl | 48.09 | 0.04 | 42.89 | 0.1 | P | Y |
| Terbutryn | 48.12 | 0.05 | 42.86 | 0.09 | P | Y |
| Chlortal dimethyl | 48.25 | 0.006 | 43.00 | 0.1 | P | Y |
| Chlorpyrifos | 48.48 | 0.001 | 43.51 | 0.07 | P | Y |
| Fenitrothion | 48.74 | 0.008 | 43.72 | 0.2 | P | Y |

Table 1 (*continued*)

| Compound | AED-C193 | | MS-SCAN | | | |
|---|---|---|---|---|---|---|
| | Retention time (min) | LOD mg/l | Retention time (min) | LOD mg/l | Peak | GC |
| Parathion ethyl | 48.89 | 0.007 | 43.92 | 0.2 | P | Y |
| Carbaryl | 48.96 | 0.2 | 43.90 | 0.5 | D | N |
| Methiocarb | 49.17 | 0.3 | 43.88 | 6 | D+ | N |
| Dichlofluanid | 49.19 | 0.006 | 43.90 | 0.1 | P | Y |
| Malathion | 49.21 | 0.001 | 44.08 | 0.2 | P | Y |
| *cis*-Heptachlor epoxide | 49.35 | 0.005 | 44.45 | 0.09 | P | Y |
| Chlorotoluron | 49.59 | 0.08 | 44.55 | 2 | D | N |
| Pirimiphos ethyl | 49.81 | 0.02 | 44.60 | 0.4 | P | Y |
| *trans*-Heptachlor epoxide | 49.88 | 0.004 | 44.67 | 0.1 | P | Y |
| Dinobuton | 49.94 | 0.02 | 44.74 | 0.7 | P | N |
| Fenthion | 50.15 | 0.03 | 45.24 | 0.3 | P | Y |
| $\gamma$-Chlordane | 50.31 | 0.004 | 45.34 | 0.1 | P | Y |
| *trans*-Nonachlor | 50.52 | 0.004 | 45.43 | 0.1 | P | Y |
| Triadimenol | 50.58 | 0.01 | 45.44 | 0.3 | M | Y |
| Bromacil | 50.65 | 0.01 | 45.52 | 0.4 | P | Y |
| Chlorbromuron | 51.14 | 0.08 | 46.06 | 2 | D | N |
| Anilazine | 51.14 | 0.02 | 46.06 | 0.5 | P | Y |
| $\alpha$-Chlordane | 51.25 | 0.002 | 46.12 | 0.1 | P | Y |
| Procymidone | 51.55 | 0.01 | 46.50 | 0.1 | P | Y |
| Endosulfan A | 51.59 | 0.009 | 46.50 | 0.08 | P | Y |
| Chlorbensid | 51.67 | 0.02 | 46.62 | 0.2 | P | Y |
| Cyanazine | 51.69 | 0.04 | 46.67 | 0.1 | P | Y |
| 2,4′-DDE | 51.71 | 0.006 | 46.77 | 0.2 | P | Y |
| Quinalphos | 52.09 | 0.01 | 47.10 | 0.4 | P | Y |
| Bentazone | 52.28 | 0.02 | 47.33 | 0.9 | D | N |
| Phentoate | 52.28 | 0.04 | 47.33 | 0.4 | P | Y |
| Dieldrin | 52.89 | 0.008 | 47.83 | 0.1 | P | Y |
| Dicofol | 52.95 | 0.004 | 48.20 | 0.2 | P | Y |
| Folpet | 53.07 | 0.01 | 48.21 | 0.5 | P | Y |
| 4,4′-DDE | 53.18 | 0.004 | 48.37 | 0.1 | P | Y |
| Metamitron | 53.58 | 0.02 | 48.78 | 0.3 | P | Y |
| Tetrachlorvinphos | 53.60 | 0.001 | 49.00 | 0.07 | P | Y |
| Captan | 53.67 | 0.02 | 48.88 | 0.2 | P | Y |
| Imazalil | 53.69 | 0.03 | 48.89 | 0.2 | P | Y |
| Thiabendazole | 54.00 | 0.09 | 49.24 | 0.9 | D | N |
| Napropamide | 54.13 | 0.01 | 49.21 | 0.1 | P | Y |
| Chlorfenson | 54.18 | 0.02 | 49.44 | 0.1 | P | Y |
| Methidathion | 54.37 | 0.03 | 49.55 | 0.2 | P | Y |
| Siduron | 54.42 | 0.3 | 50.00 | 2 | D | N |
| Endrin | 54.43 | 0.006 | 50.00 | 0.2 | P | Y |
| Fenamiphos | 54.43 | 0.01 | 50.02 | 0.3 | P | Y |
| *cis*-Nonachlor | 55.17 | 0.04 | 50.54 | 0.1 | P | Y |
| Flamprop methyl | 55.33 | 0.002 | 50.90 | 0.1 | P | Y |
| Dibenzoquat-S-methyl | 55.55 | 0.1 | 50.95 | 1 | P | N |
| Imazamethabenz methyl | 55.81 | 0.04 | 51.25 | 3 | D | N |
| Endosulfan B | 55.88 | 0.004 | 51.19 | 0.1 | P | Y |
| Fluvalinate | 55.98 | 0.0006 | 51.43 | 1 | M | Y |
| Flamprop isopropyl | 56.02 | 0.001 | 51.48 | 0.2 | P | Y |
| 2,4′-DDT | 56.02 | 0.003 | 51.39 | 0.2 | P | Y |
| 4,4′-TDE | 56.18 | 0.005 | 51.68 | 0.1 | P | Y |

(*Continued on p. 250*)

Table 1 (*continued*)

| Compound | AED-C193 | | MS-SCAN | | | |
|---|---|---|---|---|---|---|
| | Retention time (min) | LOD mg/l | Retention time (min) | LOD mg/l | Peak | GC |
| Bromoxinil octanoate | 56.48 | 0.0002 | 52.15 | 1 | P | Y |
| Picloram | 56.82 | 0.02 | 52.33 | 1 | P | N |
| Ethion | 57.08 | 0.03 | 52.75 | 0.3 | P | Y |
| 2,4'-TDE | 54.42 | 0.004 | 49.81 | 0.1 | P | Y |
| 4,4'-DDT | 57.80 | 0.005 | 53.45 | 0.1 | P | Y |
| Neburon | 57.89 | 0.2 | 53.56 | 2 | D | N |
| Carbophenothion | 58.01 | 0.05 | 53.60 | 0.3 | P | Y |
| Fensulfothion | 58.48 | 0.04 | 54.21 | 0.2 | P | Y |
| Cyhexatin | 58.60 | 0.5 | 54.28 | 2 | P | N |
| Piperonyl butoxide | 58.73 | 0.3 | 54.49 | 2 | P | N |
| Endrin aldehyde | 59.27 | 0.003 | 55.09 | 0.08 | P | Y |
| Triamiphos | 59.29 | 0.01 | 54.97 | 0.2 | P | Y |
| Triazophos | 60.27 | 0.01 | 56.18 | 0.2 | P | Y |
| Bromopropylate | 60.31 | 0.006 | 56.20 | 0.1 | P | Y |
| Iprodione | 60.53 | 0.03 | 56.49 | 0.9 | D | N |
| Fenpropathrin | 61.29 | 0.0006 | 57.28 | 1 | P | Y |
| Captafol | 61.85 | 0.01 | 57.95 | 0.3 | P | Y |
| Amitraz | 62.50 | 0.03 | 58.40 | 0.2 | P | Y |
| Methoxychlor | 62.75 | 0.03 | 58.72 | 0.2 | P | Y |
| Tetradifon | 63.22 | 0.001 | 59.15 | 0.09 | P | Y |
| Chloridazon | 63.63 | 0.03 | 59.78 | 1 | P | N |
| Phosalone | 63.79 | 0.01 | 59.93 | 0.5 | P | Y |
| Pyrazophos | 65.31 | 0.02 | 61.59 | 0.4 | P | Y |
| Prochloraz | 66.01 | 0.02 | 62.38 | 0.2 | P | Y |
| Azinphos methyl | 66.45 | 0.02 | 62.57 | 0.5 | P | Y |
| Permethrin | 66.73 | 0.0006 | 63.04 | 1 | M | Y |
| Dialifos | 67.15 | 0.03 | 63.25 | 0.3 | P | Y |
| Azinphos ethyl | 67.52 | 0.02 | 63.60 | 0.8 | P | Y |
| Coumaphos | 68.03 | 0.03 | 64.81 | 0.2 | P | Y |
| Warfarin | 69.05 | 0.04 | 65.94 | 0.4 | P | N |
| Cypermethrin | 69.58 | 0.0006 | 66.04 | 2 | M | Y |
| Fentin hydroxyde | 69.63 | 0.2 | 66.53 | 5 | P | N |
| Fenvalerate | 72.55 | 0.0004 | 69.83 | 2 | M | Y |
| Coumachlor | 73.65 | 0.01 | 69.95 | 0.6 | P | Y |
| Fenbutatin oxide | 76.03 | 0.5 | 73.69 | 9 | P+ | N |

P: One peak observed in the chromatogram.
D: Several peaks observed in the chromatogram.
M: Isomeric compound peaks observed in the chromatogram.
+: Retention time of a degradation product.
Y: Compound often analyzed by GC with hot splitless injection.
N: Compound not often analyzed by GC with hot splitless injection.
N.D.: not detected.

injected volume 2 $\mu$l; injection and transfer line temperatures, 200 and 280°C, respectively; the ion source and quadrupole temperatures were 200 and 100°C, respectively; scan range 50–500 a.m.u.; threshold 40; electron multiplier voltage was maintained 300 voltage units above autotune.

## 3. Results and discussion

### *3.1. Multiresidue analysis system*

Table 1 lists the retention times and detection limits for phytochemicals (and metabolites) of di-

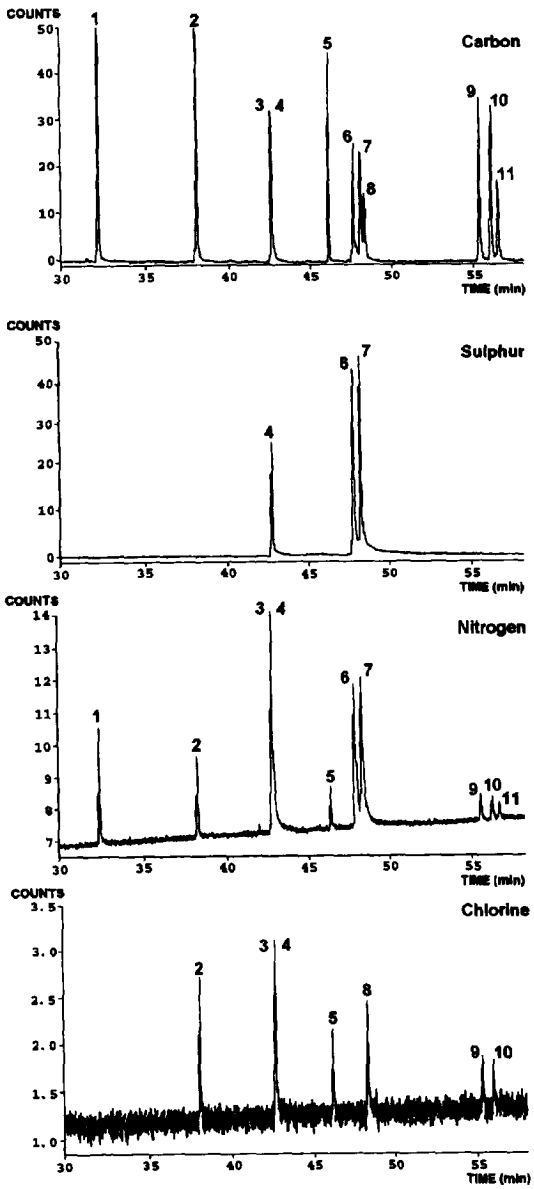


Fig. 1. Elemental chromatograms (carbon 496, sulfur 181, nitrogen 174, chlorine 479) in the atomic emission detector for a herbicide standard. See Table 4 for identification peaks.

verse agricultural use (insecticides, herbicides, fungicides, etc.) as obtained by GC–AED and GC–MS detection. The detection limits have been obtained by successive dilutions of standards, considering a signal/noise ratio of 3. The table includes some compounds, such as carbamates and ureas, whose low volatility and high thermolability characteristics make them unamenable for GC with hot splitless injection. However, the detectors assayed are responsive to these compounds which allows their presence in samples with an unknown history to be ascertained. In any case, it should be noted that these compounds have some problems in their quantitative analysis by GC [37,38]. The retention times obtained with both systems are different due mainly to the vacuum equipment used in MS, but they are linearly related ($t_{MS}=1.11t_{AED}-10.69$, correlation coefficient $r^2=0.998$), which facilitates the assignation of chromatographic peaks between both GC systems.

A distinction between the pesticides that are often determined by hot splitless injection (Y) and those which are not (N), on the basis of their physicochemical properties, is shown in the column labelled GC. This distinction was only tentative since the presence of active sites (adsorption or chemical reaction) in the chromatographic system can alter the chromatographic behavior of highly susceptible compounds such as thiabendazole and bromacil; these pesticides have only been determined with the GC–MS system in some cases. As regards the compounds not amenable to GC, Table 1 indicates the number of chromatographic peaks observed (one, P, or more, D) in the chromatogram; the pesticide named was not always present as checked by MS, probably due to thermal degradation in the injection port or chromatographic oven, which is denoted by the plus (+) sign. In such cases, the retention time given corresponds to the major degradation product or the sole compound observed. The occurrence of isomers for some phytochemicals is denoted by letter M.

The use of an AED as multiresidue system partially overcomes the problems derived from a poor resolution between some compounds. Fig. 1 shows four elemental chromatograms for the herbicide mixture subsequently studied, with atrazine and triallate co-eluting at 42.6 min, and terbutryn and chlorthal dimethyl overlapping partially at ca. 48 min. As regards the first pesticide couple, the carbon chromatogram clearly reflects their co-elution, whereas the sulphur chromatogram allows the presence of triallate to be ascertained because atrazine does not include sulphur atoms in its structure. Monitoring the nitrogen line allowed for no distinction between the two compounds since both possess

Table 2
Data obtained in the quantitation of chlorpyrifos-ethyl by the atomic emission and mass spectrometry detectors ($n=2$)

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Emission line (nm) | C | 193 | C | 496 | C | 179 | C | 248 | $^{12}C$ | 343 |
| M.D.L. ($\mu$g/l) | | 1 | | 6 | | 6 | | 4 | | 7 |
| R.S.D. (%) | | 3.1 | | 4.0 | | 3.3 | | 3.1 | | 3.5 |
| Emission line (nm) | H | 486 | H | 656 | S | 361 | S | 181 | O | 777 |
| M.D.L. ($\mu$g/l) | | 250 | | 40 | | 70 | | 40 | | 1100 |
| R.S.D. (%) | | 5.0 | | 4.8 | | 3.3 | | 3.6 | | 5.0 |
| Emission line (nm) | N | 174 | N | 348 | P | 178 | P | 186 | Cl | 479 |
| M.D.L. ($\mu$g/l) | | 75 | | 100 | | 60 | | 40 | | 100 |
| R.S.D. (%) | | 3.6 | | 3.8 | | 4.0 | | 3.3 | | 3.2 |
| Monitored masses (m/z) | | 314 | | 197+199 | | | | 197+258+314 | | |
| M.D.L. ($\mu$g/l) | | 7 | | 1 | | | | 10 | | |
| R.S.D. (%) | | 3.5 | | 3.3 | | | | 3.3 | | |

M.D.L.=minimun detectable level.
R.S.D. (%)=relative standard deviation of the fitting.

nitrogen atoms, although in very different amount (1 atom in triallate and 5 atoms in atrazine); as a result, the nitrogen response must correspond mostly to atrazine. Obviously, the use of an MS detector is necessary to confirm the presence of atrazine. Related to this subject, the observation of secondary atomic emission lines and the calculation of the elemental molar relation by GC–AED can be useful to confirm the compound identities in some cases [26,39].

The other two above-mentioned herbicides, terbutryn and chlorthal dimethyl, can be identified in a sample from the carbon chromatogram. However, greater reliability and more accurate quantitation can be achieved from the nitrogen and sulphur emission lines for terbutryn, and the chlorine emission line for chlorthal dimethyl.

Table 2 shows the minimum detected amount at a signal/noise ratio of 3 and the relative standard deviation for the linear fitting obtained with various atomic emission lines. Experiments were carried out on different solutions of the insecticide chlorpyrifos-ethyl ($C_9H_{11}Cl_3NO_3PS$), whose structure contains carbon, hydrogen, nitrogen, oxygen, sulphur and chlorine atoms, quantifying the peak height. The linearity was studied in the concentration range

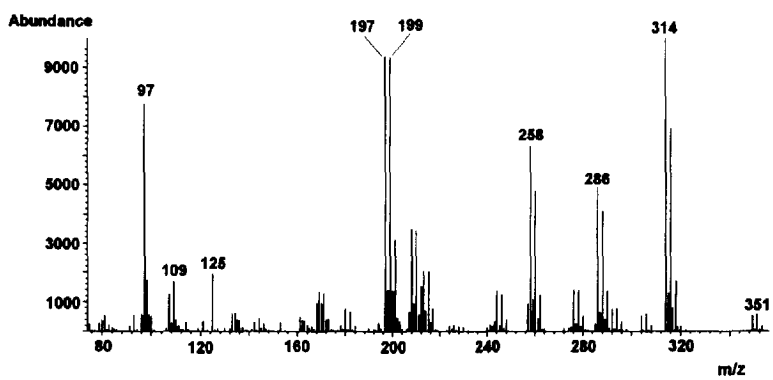


Fig. 2. Electron impact mass spectrum of chlorpyrifos-ethyl.

Table 3
Recovery and precision obtained in the extraction of herbicides with ethyl acetate from soil spiked with 0.5 mg/kg of each one ($n=5$)

| Peak[a] | Herbicide | Detection mode | Calibration curve | $r$ | Formula | Family | Recovery±R.S.D. |
|---|---|---|---|---|---|---|---|
| 1 | Propham | C193 | 4.105C+0.032 | 0.992 | $C_{10}H_{13}NO_2$ | Carbamate | 61.3±6.9 |
| 2 | Chlorpropham | C193 | 4.182C+0.016 | 0.990 | $C_{10}H_{12}ClNO_2$ | Carbamate | 72.5±6.0 |
| 3 | Atrazine | MS-EI | 0.427C+0.035 | 0.997 | $C_8H_{14}ClN_5$ | Triazine | 91.2±4.6 |
| 4 | Triallate | S181 | 474.0C+21.32 | 0.998 | $C_{10}H_{16}Cl_3NOS$ | Thiocarbamate | 91.4±5.5 |
| 5 | Alachlor | C193 | 7.312C+0.029 | 0.9991 | $C_{14}H_{20}ClNO_2$ | Acetanilide | 92.3±4.3 |
| 6 | Ametrym | C193 | 5.295C−0.593 | 0.998 | $C_9H_{17}N_5S$ | Triazine | 91.7±5.1 |
| 7 | Terbutryn | S181 | 394.5C−10.28 | 0.9994 | $C_{10}H_{19}N_5S$ | Triazine | 91.0±4.3 |
| 8 | Chlorthal dimethyl | Cl479 | 0.644C−0.286 | 0.995 | $C_{10}H_6Cl_4O_4$ | Terephthalate | 93.3±4.0 |
| 9 | Flamprop methyl | C193 | 10.14C+1.307 | 0.9996 | $C_{17}H_{15}ClFNO_3$ | Alaninate | 92.0±5.3 |
| 10 | Flamprop isopropyl | C193 | 10.55C+1.116 | 0.9994 | $C_{19}H_{19}ClFNO_3$ | Alaninate | 90.3±5.1 |
| 11 | Bromoxynil octanoate | C193 | 12.36C+0.589 | 0.9990 | $C_{15}H_{17}Br_2NO_2$ | Benzonitrile | 90.8±5.5 |

[a]Identification peaks in Figs. 1 and 3.
$r$: coefficient of regression.
R.S.D.: relative standard deviation.

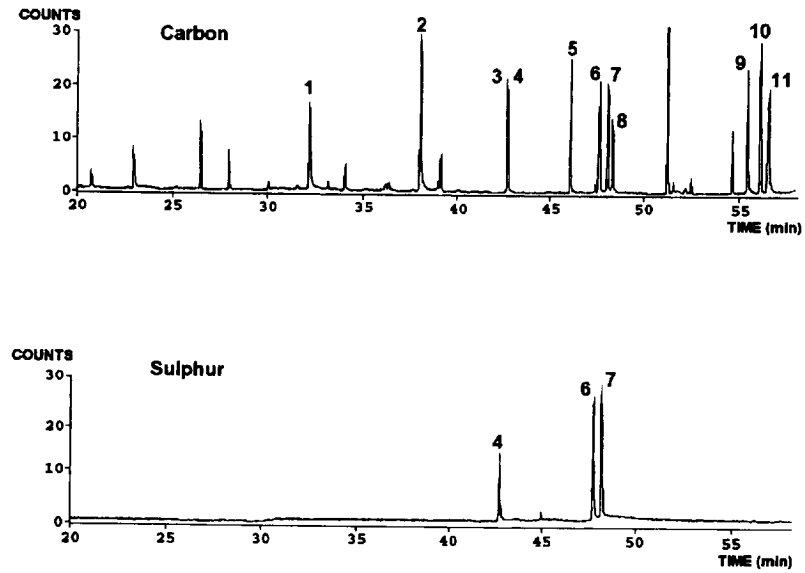


Fig. 3. Elemental chromatograms (carbon 496, sulfur 181) in the atomic emission detector for a spiked soil extract. See Table 4 for identification peaks.

between 0.15 and 10.5 mg/l in the three cases. The carbon emission lines revealed to be the most sensitive using which it was possible to measure 1 $\mu$g/l at 193 nm. The detection limits obtained with the chlorine, phosphorus and nitrogen lines were higher than those provided by selective detection methods such as ECD or NPD [34], whereas the sensitivity for sulphur was similar to that obtained by FPD. The peak height was linearly related to the concentration (with a correlation coefficient of at least 0.99) over the range 0.15–10.5 mg/l for carbon, 0.5–10.5 mg/l for hydrogen, chlorine, sulphur, phosphorus and nitrogen and 2–10.5 mg/l for oxygen.

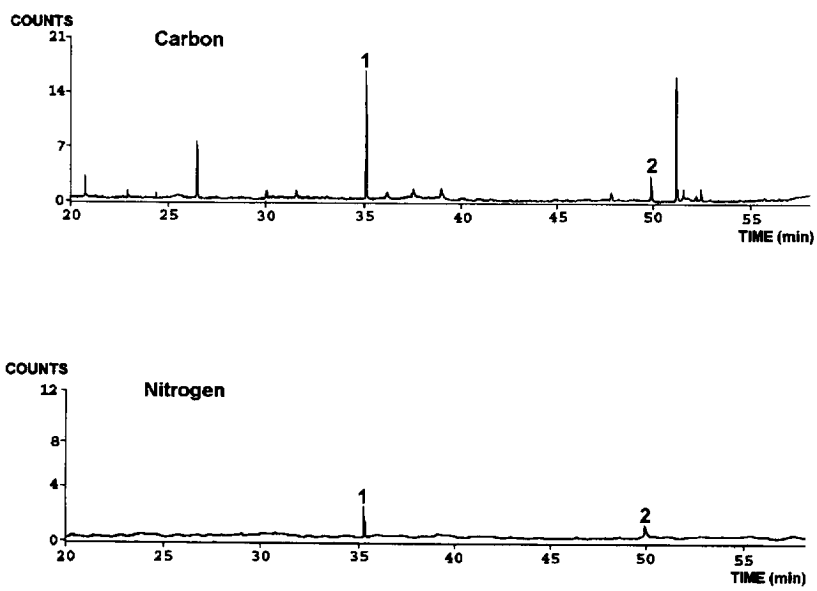


Fig. 4. Soil sample extract injected in the GC–AED system. (1) Trifluralin; (2) Chlorotoluron.

Table 2 also lists the detection limit and relative standard deviation of the fitting obtained in the quantitation of chlorpyrifos-ethyl by GC–MS in the electron impact (EI) mode by monitoring various fragment ions and making the routine instrument self-calibrating (in the midmass tune mode). The minimum amount detectable was 1 $\mu$g/l. Also, the sensitivity obtained in measuring two ions with similar $m/z$ ratios, and relative abundance close to 100%, was greater than those obtained by measuring the base ion ($m/z$ 314) and the three ions (two with relative abundance close to 100% and the third with lower abundance). In addition, it was observed that the sensitivity in measuring the base ion was slightly higher than that for the three ions as the likely result of different background noise. Fig. 2 shows the electron impact spectrum for chlorpyrifos-ethyl.

The detection limit provided by MS in the selected-ion monitoring (SIM) mode was comparable to that obtained by the carbon emission lines in the AED but lower than those achieved by monitoring the lines for the heteroatoms. The relative standard deviation of the linear fitting was also comparable for both detectors with the exception of the hydrogen and oxygen emission lines.

### 3.2. Extraction of herbicides from soil

Table 3 shows the recovery-rate and precision obtained in the extraction of 11 herbicides, including two thermolabile compounds (propham and chlorpropham), from soil using ethyl acetate as extractant and the carbon line (193 nm) for peak height quantitation. The herbicides, triallate and terbutryn, have been quantified from the sulphur emission line (181 nm), chlorthal dimethyl from the chlorine emission line, and atrazine by GC–EI-SIM-MS according to the above explanation. The fragment ion at $m/z$ 200 was monitored to quantify atrazine. In general, the results were quite acceptable, with recoveries close to 90% and relative standard deviations of about 5% ($n$=5). However, the recoveries for propham and chlorpropham were somewhat lower which cannot be ascribed to a low solubility in the extractant solvent. More likely, a degradation process through the analysis steps or in the GC system, propitiated by the presence of co-extracted substances, could be the cause. Fig. 3 shows the carbon and sulphur chromatograms for a spiked soil extract.

As regards detection limits, the method provided slightly different results depending on the particular compound and detection mode used. In any case, the method allows detection to about 0.01 mg/kg of these compounds in soil samples.

The thermolability of propham and chlorpropham is reflected in their higher detection limits, 80 $\mu$g/l, in comparison with those for the other herbicides which were below 10 $\mu$g/l, using the carbon line at 193 nm.

The multiresidue extraction procedure has been applied to the analysis of 90 soil samples devoted to cereal crops from Castile and Leon (Table 4), sampled in Spring, when the agrochemical treat-

Table 4
Pesticides and number of samples where they were found after analysis of 90 soil samples by ethyl acetate extraction

| Pesticides | Number of samples |
|---|---|
| Chlorotoluron+trifluralin | 2 |
| Trifluralin+terbutryn | 1 |
| Chlortoluron+terbutryn | 2 |
| Isoproturon+neburon | 2 |
| Terbutryn | 4 |
| Flamprop isopropyl | 3 |
| Flamprop methyl | 2 |
| Triallate | 1 |
| Trifluralin | 5 |
| Simazine | 2 |
| Atrazine | 1 |
| Chlorotoluron | 2 |
| Linuron | 1 |
| Chlorsulfuron | 3 |
| Imazamethabenz-methyl | 3 |
| Ethylenethiourea | 4 |
| Vinclozolin | 2 |
| Vinclozolin+chlorotoluron | 1 |
| Prochloraz | 1 |
| Malathion | 3 |
| Ethion | 1 |
| Endosulfan A+B | 2 |
| Lindane+HCB | 3 |
| 4,4′-DDE+2,4′ DDE | 5 |
| 4,4′-DDE+4,4′ TDE | 2 |
| 4,4′-DDE+lindane | 2 |
| 4,4′-DDE | 6 |
| 4,4′-TDE | 3 |
| Lindane | 2 |
| HCB | 1 |

ments are more frequent. Several pesticides, some of them, herbicides contained in the same commercial formulation, were identified by the GC–AED system, confirming some results by mass spectrometry. No herbicide compounds, such as organochlorine ones, have also been detected. The pesticide concentrations were in the 0.008–0.18 mg/kg range. Fig. 4 shows a chromatogram from a soil sample containing two herbicides found in the same commercial formulation.

## 4. Conclusions

AED can be used to implement a pesticide multiresidue analysis system based on GC, being very useful in the monitoring of the heteroatoms usually present in many pesticides. This results in more reliable determinations, even though MS must be used in last instance, especially to resolve overlapping. AED provides high sensitivity in its carbon line, which can be used for preliminary screening. A enrichment step of the analytes is advisable in order to selectively monitor heteroatoms at trace levels.

The GC–AED system has been satisfactorily applied to the multiresidue determination of pesticides in agricultural soils after extraction with ethyl acetate and clean-up on ODS cartridges. Acceptable recovery rate and reproducibility were obtained in the analysis of herbicides on spiked soils.

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