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The use of the electron capture detector for the analysis of volatile inorganic and organometallic compounds

A three-electrode electron capture detector (ECD) with shielding of the radioactive source by an additional inert gas stream was first suggested by GREGORY¹. For investigation of the capability of an analogous ECD for the analysis of inorganic chlorides, we used a chromatographic apparatus having two detectors: a katharometer and an electron capture detector connected in series. For the separation of compounds and the calibration of the electron capture detector, apparatus with a Teflon chromatographic column 40 cm long and 4 mm I.D. was used. The column was filled with the support "Polychrom"² with 20% (w/w) of *n*-octadecane as the liquid phase; *n*-octadecane captures few electrons and has almost no influence on the operation of the ECD. Possible reactions of the analysed compounds with the stationary phase, carrier gas, column walls and connecting lines were checked by numerous repeated introductions of pure components by means of a special pneumatic device for injecting hydrolyzable liquid samples². We did not observe any changes in the peak size and shape for individual compounds.

To take into account the diffusion of aggressive substances to the radioactive source into the shielding stream and possible tritium losses from the source³, the

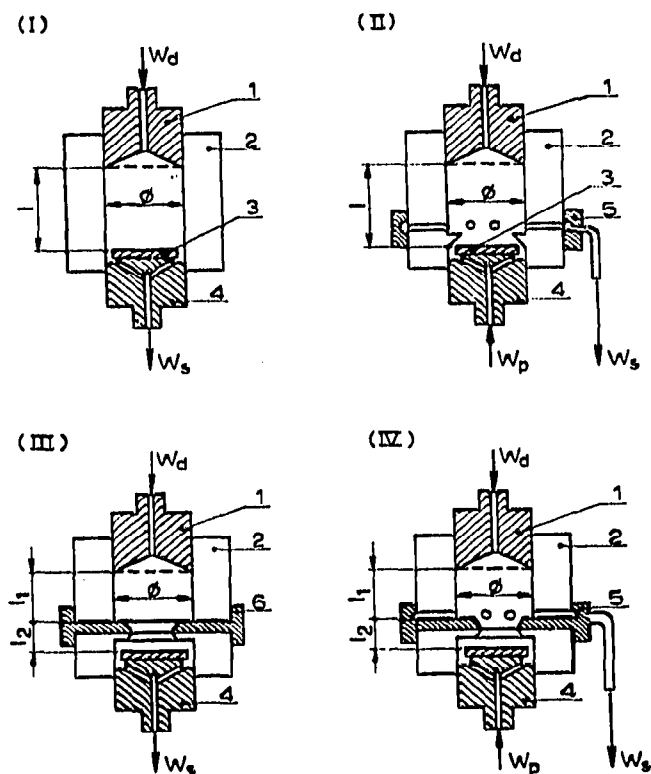


Fig. 1. Types of ECD investigated. (I) Two-electrode common type; (II) two-electrode with a shielding stream; (III) three-electrode; (IV) three-electrode with a shielding stream. 1 = Anode; 2 = insulator; 3 = radioactive source and cathode; 4 = cathode; 5 = gas collector and electrode; 6 = additional electrode. W_d = Gas flow at the detector inlet; W_p = shielding flow; W_s = flow at the detector exit; ϕ is the detector chamber diameter; l , l_1 , l_2 are the distances between electrodes.

necessary calculations for shielding stream flow-rate (W_p) were made. It was found that the flow-rate of the additional shielding stream (nitrogen) for different compounds should be 50–100 ml·min⁻¹.

The electron capture detector was investigated at constant voltage. The specifications of four types of ECD were investigated: a two-electrode, one-chamber detector without gas sweeping (type I) and with gas sweeping (type II), and a three-electrode, two-chamber detector without gas sweeping (type III) and with an additional gas stream (type IV) (Fig. 1). A comparison was made of the sensitivities of the four types of detector with optimum operation parameters. This showed that the type I ECD had the highest sensitivity. The sensitivity of the type II detector was lower than that of the type I detector. The standard current of such a two-electrode detector depends only very slightly on the flow-rate into the detector at about 40–160 ml·min⁻¹. The saturation current in the nitrogen was usually about $1 \cdot 10^{-8}$ A (tritium source maximum activity was 4.5 Ci). The maximum sensitivity for a series of chlorides (phosphorus trichloride, phosphorus oxychloride and others) is achieved at a potential of about 35 V.

An increase in the shielding stream flow-rate causes the detector sensitivity to decrease by a factor of 2–4. The detector sensitivity also decreases with an increase of the carrier gas flow-rate (W_d) through the detector when the sample size is not changed. The ECD was calibrated by a method analogous to that described by LOVELOCK *et al.*⁴, with the use of a standard solvent which does not capture electrons and a system with two detectors. The results obtained are given in Table I. Published data on the sensitivity of other detectors for the same compounds are given for comparison.

TABLE I

SENSITIVITY OF ECD TO CHLORIDES

Constant potential, 50 V. Carrier gas (nitrogen) flow-rate, 20 ml·min⁻¹; sweeping gas flow-rate, 80 ml·min⁻¹.

Compound	Minimum detectibility		Katharometer, carrier gas		Flame-photometric detector ^{5,6}	Thermionic detector ⁷
	ECD		gas		Moles	$g \cdot sec^{-1}$
	Moles	$g \cdot sec^{-1}$	Nitrogen (moles)	Helium (moles)		
SiCl ₄	$2.9 \cdot 10^{-12}$	$4.0 \cdot 10^{-11}$	$1.9 \cdot 10^{-6}$	$1.5 \cdot 10^{-8}$	$4 \cdot 10^{-11}$	$1 \cdot 10^{-10}$
GeCl ₄	$6.5 \cdot 10^{-10}$	$4.7 \cdot 10^{-9}$	$2.8 \cdot 10^{-6}$	$1.8 \cdot 10^{-8}$	—	$1 \cdot 10^{-9}$
SnCl ₄	$3.1 \cdot 10^{-8}$	$1.1 \cdot 10^{-7}$	$1.1 \cdot 10^{-6}$	$6.9 \cdot 10^{-8}$	$7 \cdot 10^{-9}$	$1 \cdot 10^{-10}$
PCl ₃	$1.7 \cdot 10^{-12}$	$1 \cdot 10^{-11}$	$8.7 \cdot 10^{-7}$	$4.0 \cdot 10^{-8}$	$2 \cdot 10^{-9}$	$1 \cdot 10^{-10}$
POCl ₃	$1.6 \cdot 10^{-11}$	$8.3 \cdot 10^{-11}$	$6.8 \cdot 10^{-6}$	$1.6 \cdot 10^{-7}$	—	—
PSCl ₃	$5.9 \cdot 10^{-11}$	$1.0 \cdot 10^{-10}$	$8.1 \cdot 10^{-6}$	$1.5 \cdot 10^{-7}$	—	—
CCl ₄	—	$9 \cdot 10^{-13}$	$1.5 \cdot 10^{-6}$	—	—	$2.7 \cdot 10^{-11}$

Based on the data in Table I for tetrachlorides, the dependence of the detector response on the position of the central atoms in the Periodic Table was found (Fig. 2). The linear dependence is possibly connected with the influence of the metal atom on electron capture and consequently on detector response. A sensitivity decrease in the

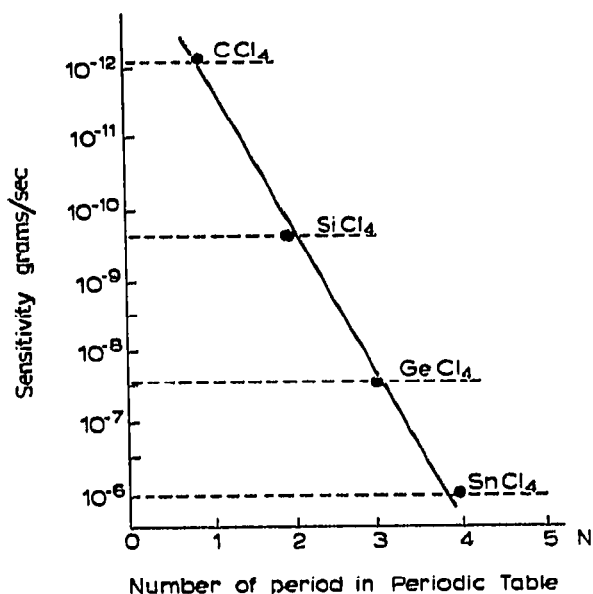


Fig. 2. Dependence of ECD sensitivity on the position of the element in the Periodic Table.

series carbon tetrachloride to tin(IV)chloride can be accounted for by an increase in the ionization of the bond in the compound. Because of this, the possibility of capture decreases. In the case of tin(IV)chloride, a rather low ECD sensitivity was obtained (almost the same sensitivity as with the katharometer when helium was used as carrier gas).

By using the data obtained in an apparatus with two detectors, the analyses of metal chlorides containing micro-impurities were carried out. In this case, it is

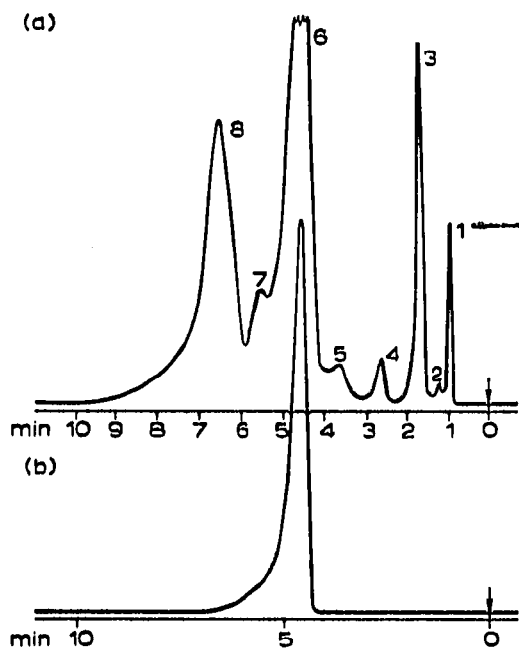


Fig. 3. Chromatogram of tin(IV) chloride analysis, (a) with ECD; (b) with katharometer. Column with 20% of *n*-octadecane on a Teflon type support, "Polychrom". Carrier gas, nitrogen at a flow-rate of $27.2 \text{ ml} \cdot \text{min}^{-1}$. Temperature, 120°C . Peaks: 1 = HCl ; 2 = unidentified; 3 = SiCl_4 ; 4 = $(\text{CH}_3)_4\text{Sn}$; 5 = unidentified; 6 = SnCl_4 ; 7 = unidentified; 8 = $(\text{CH}_3)_3\text{SnCl}$.

possible to determine about 10^{-6} % of silicon tetrachloride and 10^{-7} % of phosphorus trichloride. All the other compounds can be detected when they are present in a sample at a concentration of about 10^{-4} %. For example, by using an ECD, five impurities, namely hydrogen chloride, silicon tetrachloride, tetramethyltin and trimethyltin chloride, were detected in tin(IV) chloride purified on a rectification column. The concentration of silicon tetrachloride was 10^{-6} % (Fig. 3). The chromatogram of the tetramethyltin analysis with the ECD and katharometer is given in Fig. 4.

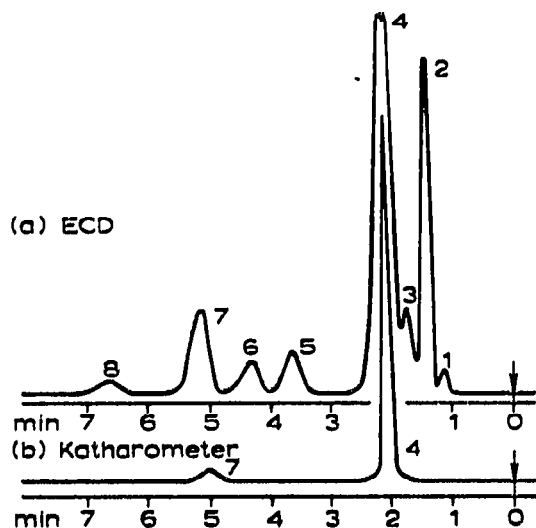


Fig. 4. Chromatogram of the tetramethyltin analysis with ECD and katharometer. Katharometer: bridge current, 150 mA; attenuator, 1:10; recorder, 1 mV; carrier gas, nitrogen. ECD: D.C. potential, 50 V; attenuator, 1:10; recorder, 10 mV; gas flow-rate in the detector, 80 ml \cdot min $^{-1}$; sweeping gas flow-rate, 80 ml min $^{-1}$. Other experimental conditions as in Fig. 3. 1 = HCl; 2 = $(\text{CH}_3)_4\text{Ge}$; 3 = SiCl_4 ; 4 = $(\text{CH}_3)_4\text{Sn}$; 5 = $(\text{CH}_3)_3\text{GeCl}$; 6 = unidentified; 7 = SnCl_4 ; 8 = $(\text{CH}_3)_3\text{SnCl}$.

Thus an ECD with an inert gas stream shielding the radioactive source is suitable for use with reactive compounds. Although the investigation of the operation of the ECD was carried out with a comparatively small number of compounds, the results obtained showed the possibility of the use of such detectors for the highly sensitive detection of halogen-containing inorganic and organometallic compounds.

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