

Non-radioactive electron capture detector based on X-ray ionization for the detection of pollutants

Maximilian J. Kueddelsmann, Erik Bunert und Stefan Zimmermann

*Leibniz University Hannover, Institute of Electrical Engineering and Measurement Technology,
Department of Sensors and Measurement Technology, Appelstr. 9A, 30167 Hannover, Germany*

Contact: Kueddelsmann@geml.uni-hannover.de

Introduction

For analyzing complex mixtures of electron-affine substances by gas chromatography (GC), electron capture detectors (ECD) are preferably used as highly sensitive GC-detectors. ECDs are characterized by their fast response, high linearity of up to four orders of magnitude and detection limits in the ppt_v-range. GC-ECDs are consequently highly suitable for the analysis of pesticides or other environmental toxins, making GC-ECDs standard instruments in many analytical laboratories [1–3]. In general, high energetic electrons from a radioactive ^{63}Ni source ionize nitrogen in the ECD reaction region to generate a large number of free (secondary) electrons. In the presence of electron-affine substances, the electrons can be captured and the number of free electrons reduces. Thus, the number of free electrons is a measure for the concentration of electron-affine substances. The number of free electrons is measured by applying an electric field guiding the free electrons to a Faraday detector, which is connected to a current amplifier. The high difference in mobility between the free electrons and the ionized electron-affine substances ensures that only the electrons reach the detector if the reaction region geometry and operating parameters are selected appropriately. The negative ions, instead, substantially recombine with the positive ions or leave the reaction region in the gas stream before reaching the detector electrode [4].

As shown by Maggs et. al [5], an increase in sensitivity and linearity is achieved by using short voltage pulses to move all free electrons to the detector. Therefore, the frequency is regulated in such a way that the average detector current is kept constant. In this constant current mode, an increasing substance concentration consequently requires a higher pulse frequency, so that the measured electron quantity per time is kept constant.

Up to now, radioactive β -emitters such as ^{63}Ni have been used to ionize a carrier gas like nitrogen to generate the free, thermalized electrons. However, due to legal regulations with respect to handling and disposing radioactive materials, ECDs are replaced by costly and bulky mass spectrometers, despite their

outstanding linearity and sensitivity. Furthermore, in many environmental applications, separation by GC is sufficient and the additional structural information provided by mass spectrometry is not required. In this work, we present an electron capture detector based on low energetic X-ray ionization to generate free electrons in nitrogen.

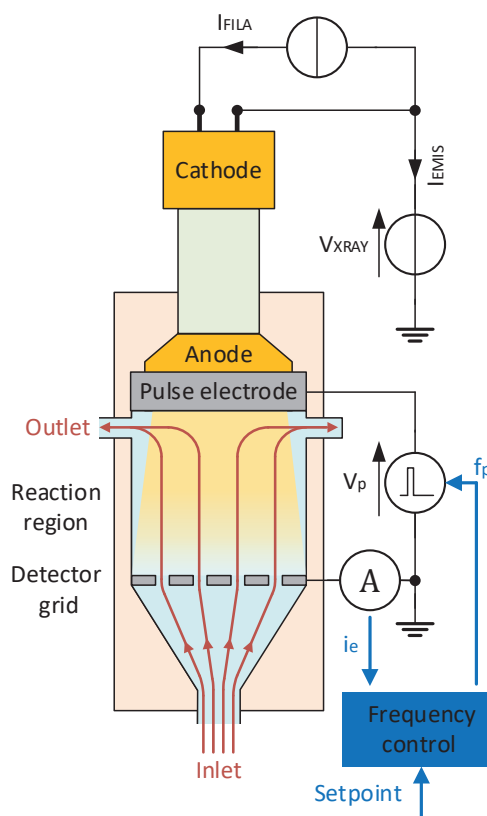


Fig. 1: Schematic of the X-ray based electron capture detector (X-ECD) operated in constant current mode.

This new X-ray based electron capture detector (X-ECD) has similar performance to radioactive electron capture detectors but is not or less restricted by legal regulations.

Experimental

Fig. 1 shows a schematic of the X-ECD operated in constant current mode. Instead of high-energetic primary electrons from a radioactive β -emitter, a small X-ray tube (40 mm length with a 10 mm diameter) with an accelerating voltage $V_{\text{XRAY}} = 4.95$ kV for generating soft X-rays is used to ionize the GC carrier gas, here nitrogen. Thus, a large number of free secondary electrons in a thermalized state are available for electron capture reactions [6]. The anode with its metallic X-ray exit window together with a metallic mount forms the pulse electrode, as shown in the schematic diagram in Figure 1, and ensures uniform ionization in the cylindrical reaction region with a diameter of 8 mm. The Faraday detector, here in form of a stainless-steel grid, is placed 7 mm away from the pulse electrode on the opposite of the reaction region and is connected to a current measuring amplifier. The analyte vapor enters the reaction region through the Faraday detector grid and flows uniformly distributed to the outlet at the pulse electrode. All further components are made of the chemically inert polymer polyether ether ketone (PEEK).

For a better sensitivity and linearity, the X-ECD is operated in constant current mode. First, the generation of free, thermalized electrons and the capture reactions of electrons by electron-affine analyte molecules run without the influence of an electric field. Afterwards, a short voltage pulse between the pulse electrode and the detector grid is applied to move the remaining electrons to the detector. Due to a low-pass behavior of the current measuring amplifier (a custom-built transimpedance amplifier with a gain of 334 M Ω and a bandwidth of 77 Hz), the electric current is averaged at hardware level.

The output signal of the current measuring amplifier is further fed to an analog pulse frequency control, which directly adjusts the pulse frequency so that the desired detector current remains constant at a defined value. The pulse frequency control can operate between pulse frequencies of 2.2 kHz and 190 kHz with pulse widths between 0.4 μ s and 2.2 μ s and voltage levels of up to 60 V. However, it is also possible to deactivate the pulse frequency control and set a fixed pulse frequency as used for further experimental characterization of the X-ECD.

All concentration sweeps were set in a pyramid pattern, so the number of increasing and decreasing concentration steps is equal. Thus, memory effects or other long-time drift effects can be easily identified through systematic differences between the in- and decreasing measuring points. To generate a constant analyte vapor concentration, the analyte is filled into a permeation vial heated to 35 °C in a well-controlled

permeation oven (VICI Dynacalibrator Model 150). The permeation oven is pressure controlled und constantly purged with a flow of 600 ml/min of nitrogen. For low analyte concentrations, an adjustable fraction of this gas can be diluted with further nitrogen. For the adjustment of all gas flows, mass flow controllers of the EL-FLOW Select series from Bronkhorst were used. All used substances were purchased from Sigma Aldrich with purities over 99%.

For a first characterization of the X-ECD to determine the optimal operating parameters, as well as sensitivity and linearity, the analyte vapor was fed directly into the reaction region. Based on these results the X-ECD was then coupled to a commercial Agilent 7890A GC to evaluate the X-ECD as a GC-detector. The used column was a 30 m long Rtx-CLPesticides with an inner diameter of 250 μ m and a film thickness of 0.25 μ m. The oven temperature program ramped from 50 °C with 20 °C/min to 200 °C (hold 5 min). Nitrogen was used with 0.63 ml/min gas flow through the GC column in the constant flow mode. Optionally, a make-up gas (nitrogen) can be added to increase the gas flow through the reaction region. A passivated transfer capillary with a temperature of 100 °C was used to connect the GC column to the X-ECD. The X-ECD itself was not heated and operated at 21 °C for all measurements.

This paper is intended to demonstrate preliminary results and thus validate the basic concept. Therefore, a detailed error calculation or a repetition of measurements in sufficiently high number for the indication of error bars in single measurements has been omitted.

Results

First, the optimum operating parameters of the X-ECD have to be specified. Therefore, the pulsed collector voltage, the pulse width and the gas flow have to be selected carefully, so that all remaining free electrons reach the detector per pulse, while the negative ions recombine or leave the reaction region without reaching the detector.

Starting with the pulsed collector voltage, a limiting voltage level can be observed even without any electron generation by the X-ray tube. Fig. 2 shows that a significant current is measurable above a pulsed collector voltage of 30 V for different pulse frequencies even without free electrons present in the reaction region.

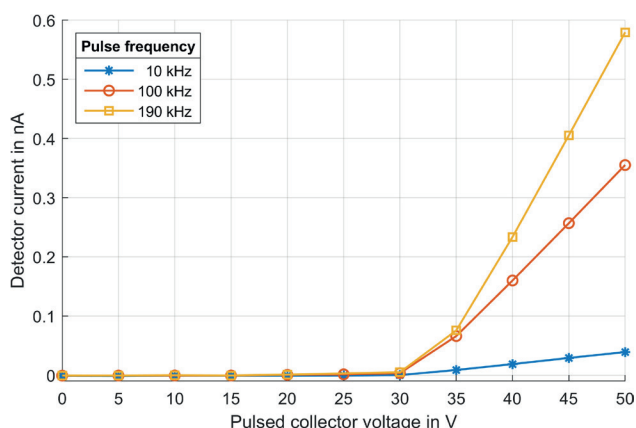


Fig. 2: Detector current over pulsed collector voltage with switched off X-ray tube and a pulse width of 1 μ s to evaluate possible interfering capacitive couplings.

This can be explained as follows. Voltage pulses above 30 V cause such a high capacitive coupled interference due to the parallel electrode arrangement, which can no longer be compensated by the current measuring amplifier. An influence of the pulse width could not be found. In general, it is advantageous for higher linearity to use a minimal pulse width in order to increase the time for electron generation and electron capture reactions between two pulses. Consequently, for a given electron mobility, the maximum possible collector voltage should be used to move all free electrons to the detector in shortest time. Therefore, a pulse voltage of 30 V is selected for the following measurements to ensure that only the electron current is measured for the entire pulse frequency range.

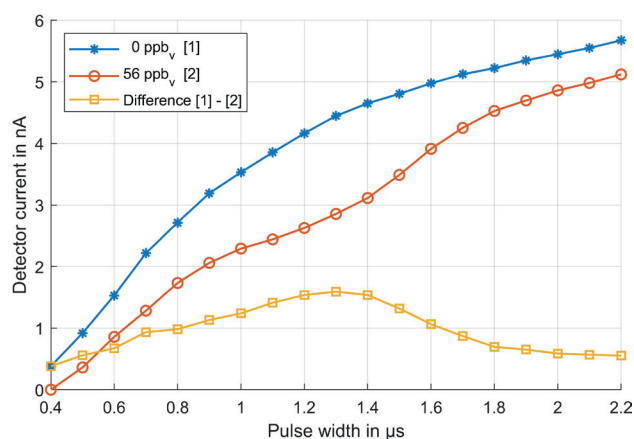


Fig. 3: Detector current over pulse width with and without an electron-affine substance present in the reaction region, here 56 ppb_v 1,1,2-trichloroethene, at a pulsed collector voltage of 30 V, a fixed pulse frequency of 190 kHz, a nitrogen gas flow of 15 ml/min and maximal X-ray intensity ($V_{\text{XRAY}} = 4.95$ kV, $I_{\text{EMIS}} = 95$ μ A). Also the difference between the two measurements without and with 1,1,2-trichloroethene.

For selecting the optimal pulse width, the pulse width has been varied with and without the addition of an electron-affine model substance (56 ppb_v 1,1,2-trichloroethene, CAS number 79-01-6) to the gas flow, as shown in Figure 3, while the pulse frequency and X-ray intensity were set to maximum ($V_{\text{XRAY}} = 4.95$ kV and $I_{\text{EMIS}} = 95$ μ A).

Without the addition of an electron affinity substance to the nitrogen, the detector current steadily increases for increasing pulse widths. For higher pulse widths, the increase becomes almost linear. In this region, in addition to the accumulated electrons, electrons formed during the pulse are also moved directly to the detector, of which a certain proportion would otherwise recombine during the accumulation phase. This leads to an almost linear increase of the detector current. However, the amount of electrons resulting in a detector current of 5.7 nA for a pulse width of 2.2 μ s shows a satisfying ionization efficiency of the X-ray tube. ECDs with radioactive ^{63}Ni source for example show similar detector currents [7,8].

When 1,1,2-trichloroethene is present, the detector current is significantly lower at each pulse width caused by the electron capturing process. The difference between the two curves shows a maximum at a pulse width of 1.3 μ s. This suggests that for pulse widths above 1.3 μ s, increasingly more negative ions reach the detector, whereby the fundamental measurement effect of the electron-ion separation decreases. To ensure that no ions reach the detector while most of the free electrons are moved to the detector, a pulse width of 1.2 μ s is selected for the further measurements.

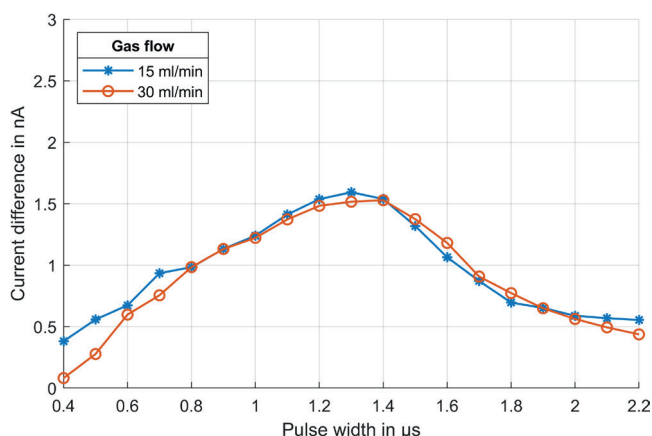


Fig. 4: Difference of the detector current over pulse width according to Fig. 3 for two different gas flows.

Finally, the gas flow is investigated. Fig. 4 shows that even doubling the gas flow through the reaction region does not affect the height and position of the difference maximum from Fig. 3.

This is consistent with the fundamental ECD studies of Wentworth et al. [9] from 1966, according to which the recombination of negative and positive ions (10^5 to 10^8 times faster than the recombination of electrons and positive ions [4]) and not the velocity of the ions through the gas flow out of the reaction region is crucial. Thus, the X-ECD shows a concentration-sensitive and not mass-sensitive behavior when operating in constant current mode. Nevertheless, a more detailed investigation of lower gas flows especially in the GC-typical range of only a few ml/min will be part of future investigations.

Based on the optimum operating parameters, the sensitivity and linearity of the X-ECD for 1,1,2-trichloroethene is now investigated while the analyte vapor is still introduced directly into the reaction region. The X-ECD operated in constant current mode with automated pulse frequency control. Fig. 5 shows the relative pulse frequency change with increasing concentration while the detector current is set to 3 nA.

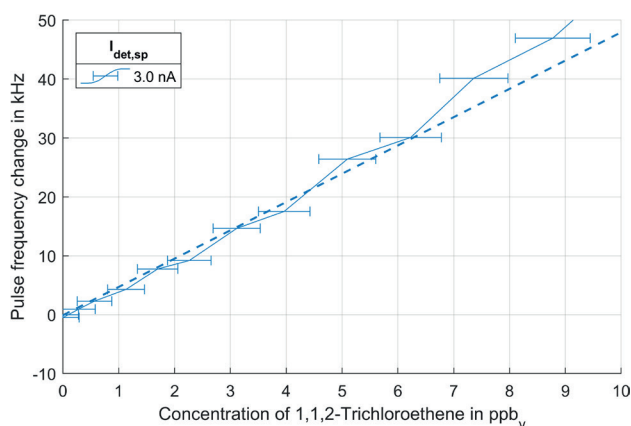


Fig. 5: Relative pulse frequency change over 1,1,2-trichloroethene concentration at a fixed detector current ($I_{\text{det,sp}}$) of 3 nA, a pulse voltage of 30 V, a pulse width of 1.2 μs , and a gas flow of 15 ml/min. The horizontal error bars represent the adjustment errors of the used mass flow controllers.

The change in pulse frequency shows a linear behavior with a sensitivity of about 5 kHz/ppb_v, which differs from the linear regression by less than 5% up to the linearity limit concentration of 6.3 ppb_v. When the pulse frequency is averaged over 200 ms, the standard deviation of the pulse frequency is $\sigma = 9$ Hz, which results in a calculated detection limit (3σ -definition) of 5 ppt_v, which compares well to radioactive ECDs. The lowest concentration measured was 280 ppt_v. The achieved linearity as the ratio of the linearity limit concentration and the detection limit is thus slightly above 3 orders of magnitude with $1.26 \cdot 10^3$ for 1,1,2-trichloroethene. One option to further increase the linearity of radioactive ECDs is using an argon-methane mixture as carrier gas to bring

the electrons faster into a thermalized and thus more favorable energy level for the electron capture process [9,10]. Whether this is the case for electrons generated by X-rays needs to be clarified in future investigations.

Fig. 6 contains the measurement from Fig. 5 over a wider concentration range and shows that after leaving the linear range there is an increase in sensitivity.

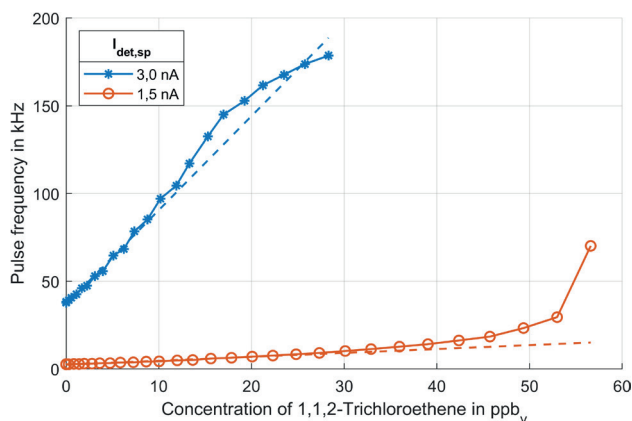


Fig. 6: Pulse frequency over 1,1,2-Trichloroethene concentration at two different fixed detector currents ($I_{\text{det,sp}}$) of 1.5 nA and 3 nA, a pulse voltage of 30 V, a pulse width of 1.2 μs and a gas flow of 15 ml/min.

The increasing concentration leads to an exhaustion of available free electrons, so that the controller must answer with a disproportionate increase in pulse frequency in order to reach the defined detector current with the few remaining electrons. For such high pulse frequencies, however, the time between two pulses and thus the possible reaction time for electron capture reactions decreases to such a degree that no free electrons are captured even with further increasing concentration, so that the pulse frequency stagnates again. In addition, at a pulse frequency of 180 kHz, the pulse width of 1.2 μs is already approx. 22 % of the pulse period. The detector current thus also consists to an increasing extent of electrons, which are formed during the pulse and therefore are directly pulled to the detector.

If a detector current of 1.5 nA instead of 3 nA is set, a much lower pulse frequency is initially required to reach the detector current without any 1,1,2-trichloroethene in the reaction region. Furthermore, the current can now be reached even at high concentrations with the remaining electrons by less pulse frequency increase. The lower sensitivity of 0.23 kHz/ppb_v results in a higher limit of detection of about 120 ppt_v, but also in a higher linearity limit concentration of now 25 ppb_v. Thus, by selecting the detector current, the absolute linearity range can be selected depending on the measurement purpose.

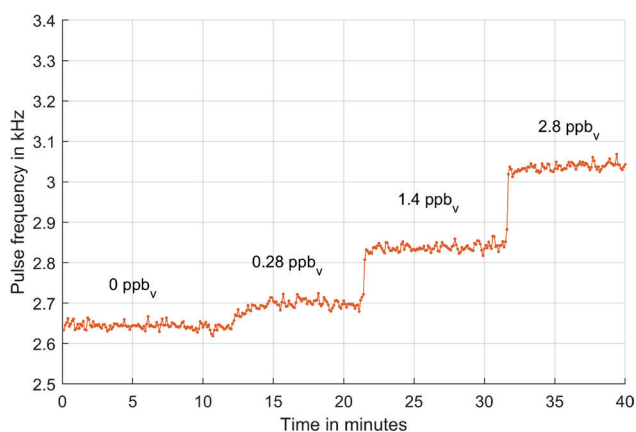


Fig. 7: Pulse frequency for different 1,1,2-trichloroethene concentrations at a fixed detector current of 1.5 nA, a pulse voltage of 30 V, a pulse width of 1.2 μ s and a gas flow of 15 ml/min. The X-ECD has a limit of detection of about 120 ppt_v for these parameters.

The stability of the measurement signal for single concentration steps is shown in Fig. 7 for a fixed detector current of 1.5 nA. Over a range of several minutes no drift can be observed. Only the first step shows a longer saturation curve, which, however, can be explained by the initial saturation of all feed lines when the analyte is added the first time.

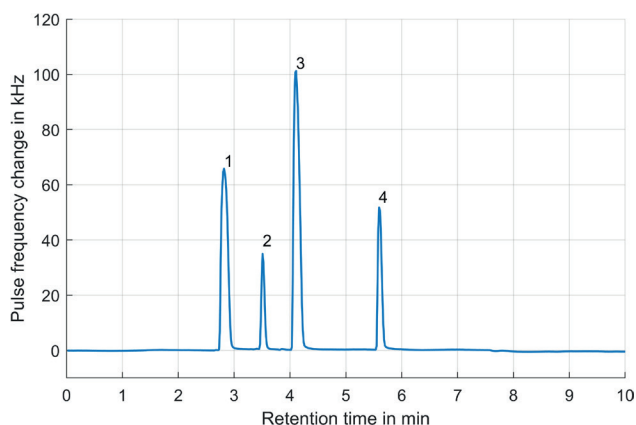


Fig. 8: Gas chromatogram of (2) 0.3 ng 1,1,2-trichloroethene, (3) 0.3 ng tetrachloroethene and (4) 3 ng 1,3-dichlorobenzene in (1) methanol as solvent, with an Agilent 7890A GC using a Rxt-CLPestizides GC column, 0.63 ml/min (20 cm/s) nitrogen carrier gas flow (constant flow mode), nitrogen make-up-gas of 14 ml/min, 1:20 split injection at 250 °C, oven temperature of 50 °C to 200 °C with 20 °C/min (hold 5 min), pulsed collector voltage of 30 V with pulse width of 1.2 μ s and detector current of 1.5 nA.

Finally, for demonstration, the X-ECD is coupled to a commercial gas chromatograph from Agilent (7890A). Fig. 8 shows a first gas chromatogram of: (1) methanol (solvent), (2) 0.3 ng 1,1,2-trichloroethene, (3) 0.3 ng tetrachloroethene and (4) 3 ng 1,3-

dichlorobenzene as test substances. The X-ECD is able to detect the injected halogenated hydrocarbons in the selected GC setup with an appropriate peak shape. The gentle tailing of the peaks is probably a result of the unheated X-ECD. The X-ray tube and the used polymer of the X-ECD can in principle be operated at up to 250 °C. Thus, a suitable heating concept will be developed in the near future.

Conclusion

In this paper, we present the X-ECD - a new electron capture detector based on the generation of electrons through X-ray ionization of nitrogen. The exemplary measurement of 1,1,2-trichloroethene in nitrogen shows a linearity of slightly more than 3 orders of magnitude and a limit of detection of 5 ppt_v, which compares well with radioactive ECDs. The operating parameters were a pulse width of 1.2 μ s, a pulsed collector voltage of 30 V, a fixed current of 3 nA and a gas flow of 15 ml/min. Furthermore, the X-ECD shows excellent performance as a GC detector demonstrated by separating three exemplary halogenated pollutants by coupling the X-ECD to a commercial GC (Agilent 7890A). Thus, the presented X-ECD is a promising alternative to radioactive ECDs. Future work focusses on a proper heating concept.

Acknowledgment

We thank AMA Instruments GmbH for their help during this work.

References

- [1] F. Barani, N. Dell'Amico, L. Griffone, M. Santoro, C. Tarabella, Determination of Volatile Organic Compounds by Headspace Trap, *Journal of Chromatographic Science* 44, 625–630 (2006); doi: 10.1093/chromsci/44.10.625.
- [2] E. C. M. Chen, E. S. Chen, Electron affinities from gas chromatography electron capture detector and negative ion mass spectrometry responses and complementary methods, *Journal of Chromatography A*, 1–17 (2018); doi: 10.1016/j.chroma.2018.08.041.
- [3] J. E. Lovelock, S. R. Lipsky, Electron Affinity Spectroscopy—A New Method for the Identification of Functional Groups in Chemical Compounds Separated by Gas Chromatography, *Journal of the American Chemical Society* 82, 431–433 (1960); doi: 10.1021/ja01487a045.
- [4] E. D. Pellizzari, Electron capture detection in gas chromatography, *Journal of Chromatography A* 98, 323–361 (1974); doi: 10.1016/S0021-9673(00)92077-6.

- [5] R. J. Maggs, P. L. Joynes, A. J. Davies, J. E. Lovelock, Electron capture detector. New mode of operation, *Analytical Chemistry* 43, 1966–1971 (1971); doi: 10.1021/ac60308a014.
- [6] T. Reinecke, A. T. Kirk, A. Heptner, D. Niebuhr, S. Bottger, S. Zimmermann, A compact high-resolution X-ray ion mobility spectrometer, *Review of Scientific Instruments* 87, 53120 (2016); doi: 10.1063/1.4950866.
- [7] J. E. Lovelock, A sensitive detector for gas chromatography, *Journal of Chromatography A* 1, 35–46 (1958); doi: 10.1016/S0021-9673(00)93398-3.
- [8] P. G. Simmonds, D. C. Fenimore, B. C. Pettitt, J. E. Lovelock, A. Zlatkis, Design of a nickel-63 electron absorption detector and analytical significance of high-temperature operation, *Analytical Chemistry* 39, 1428–1433 (1967); doi: 10.1021/ac60256a020.
- [9] W. E. Wentworth, E. Chen, J. E. Lovelock, The Pulse-Sampling Technique for the Study of Electron-Attachment Phenomena, *The Journal of Physical Chemistry* 70, 445–458 (1966); doi: 10.1021/j100874a021.
- [10] E13 Committee, Practice for Use of Electron-Capture Detectors in Gas Chromatography (2011).