DOI 10.5162/14dss2019/2.4

New Non-Radioactive Field Emission based Electron Source for Electron Capture Detectors

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Introduction

Since the introduction of the Electron Capture Detector (ECD) by Lovelock and Lipsky more than 60 years ago, ECDs have become one of the most sensitive and thus most important detectors in gas chromatography for the detection of electron affine substances like halogens and chlorofluorocarbons [1]. Such compounds can be found in many hazardous chemicals such as pesticides. Although sensitivity and linearity of ECDs have been improved over time the principal of operation is still the same [2–4]. Free electrons generated by a radioactive electron source, such as ^{63}Ni, are captured by electron affine analyte molecules reducing the number of free electrons, which otherwise reach the detector electrode inside the ECD [1]. This current reduction is the primary detector signal, which is related to the concentration of analytes in the sample [1–4]. The radioactive electron source is easy to employ and does not need any external power supply or maintenance. However, legal restrictions apply on sale, usage, and disposal of radioactive sources, which increase the total cost of ownership by a significant amount.

Hence, a strong demand exists to replace radioactive electron sources in ECDs. Therefore, the research and development of non-radioactive electron sources for ECDs is an ongoing task for many years. However, just two solutions among several other attempts stood up. One approach is to generate free electrons through a pulsed helium discharge [3]. Nevertheless, this approach only entered a niche market due to its high instrumental effort and operating costs. The other and more recent approach is to emit electrons from a hot filament in a vacuum chamber using thermionic emission and to accelerate those electrons for transmission through a thin gas-tight membrane to ambient pressure [4–8]. In other applications like ion mobility spectrometry (IMS) such electron sources have been successfully used since years [8–13]. We recently introduced a novel non-radioactive ECD [4] using our thermionic electron source offering a high linearity of up to $6.5 \cdot 10^3$ and a limit of detection (LoD) as low as 2 ppb_v in the pulsed operating mode for 1,1,2-trichlorethane. Those specifications compare well to classical radioactive ECDs [4,12].

Another way of generating free electrons in a vacuum chamber is field induced electron emission with some benefits regarding the driver electronics and energy consumption, but also some drawbacks regarding the electron emission stability requiring advanced electron emission control circuits. Here, we investigate such a field emission based electron source and its application in ECDs for the first time. Fig. 1 shows the new electron source that also has a significantly increased membrane for transmitting the accelerated electrons to ambient pressure. Such an increased membrane area reduces the electron density and thus prevents excessive Coulomb repulsion. Furthermore, the membrane material is conductive to avoid any charging effects. Field emission is based on quantum tunneling of electrons in a strong electric field (>10^9 V/m). The current density is described by the Fowler-Nordheim-equations, which are highly non-linear [14,15]. The electric field is created by applying an extraction voltage between the structured emitter and the extraction grid positioned above the field emitter. The field emission current is mainly dependent on the electric field strength. The distance between the emitter and the extraction grid needs to be minimized to create high electric field strengths with low extraction voltages. The local electric field strength can be significantly increased by using thin needle like or sharp structures which enhance the electric field by condensing the field lines [14–16].

Therefore, the KETEK GmbH and the OTH Regensburg developed an emitter chip with a needle shaped black silicon structure on top of an array of pillars, as shown in Fig. 2. Fitted with a silicon extraction grid, emission currents of up to several µA with extraction voltages below 1 kV could be achieved. The new field emission based electron source, shown in Fig. 1, consists of the emitter chip and the extraction grid contained in a compact vacuum-sealed metal package Ø 22 x 34 mm.

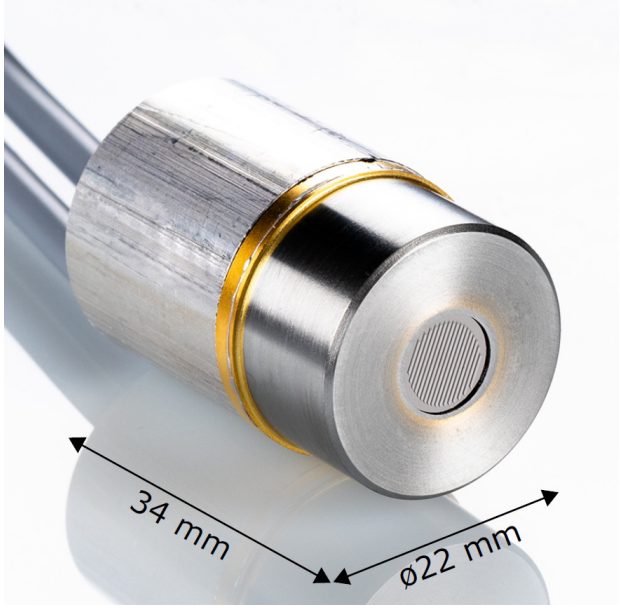

Fig. 1: Photo of the non-radioactive electron emitter based on field emission [KETEK GmbH].

The metal package serves as the anode for the acceleration voltage while the emitter and the grid are mounted on an isolated standoff inside the package. The use of a conductive package is beneficial to avoid any charging effects. The emitter chip and the extraction grid are connected via isolated electrical feedthroughs to the control electronics. The thickness and the diameter of the membrane play a major role in the effective emission current. For high and constant electron transmission, a new conductive membrane is used to avoid any charging effects [7]. The 150 nm thin and 7 mm wide pyrolytic carbon membrane with a silicon support structure enables electron transmission starting at an acceleration voltage of just 2.2 kV. The membrane has a geometrical efficiency of 86.5 % meaning that just 13.5 % of the membrane area are covered by the support structure.

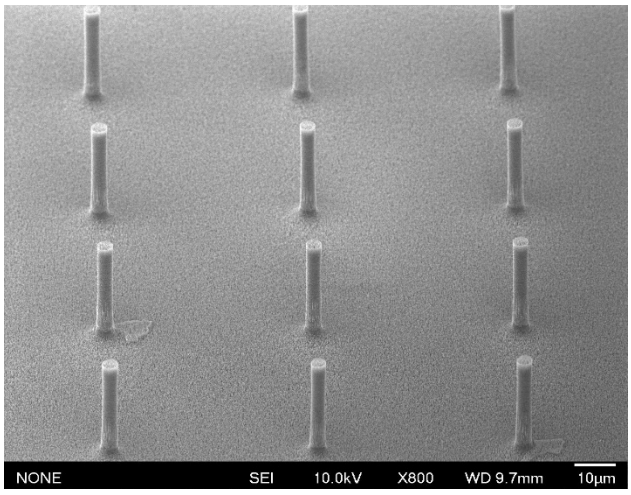

Fig. 2: SEM image of a silicon field emitter array [KETEK GmbH, OTH Regensburg].

While being just 150 nm thin the membrane can withstand up to 2 bar of differential pressure. Due to the highly non-linear characteristic curve of a field emission based electron source an advanced control system is required to keep a constant emission current. The source control electronics developed by the KETEK GmbH allow to set the acceleration voltage thus the maximum electron energy and the extraction voltage as well as to adjust the emission current [17].

Experimental Setup

The new field emission based electron source is coupled to our previously presented ECD [4] as shown in Fig. 3. The ECD is used in a pulsed operating mode for high linearity by applying a collector voltage with a fixed pulse width to pull free electrons inside the ECD measuring chamber onto the faraday detector [2,4]. The so generated detector current is amplified and converted into a proportional voltage signal by a transimpedance amplifier developed and adapted at our institute [18]. The signal is fed into the ECD control electronic previously presented in [4], which regulates the pulse frequency to keep the detector current at a set level. That way, the pulse frequency is proportional to the analyte concentration [2,4]. The ECD control electronic gives a frequency proportional voltage, which is sampled by a Keysight 34461A bench multimeter with an aperture time of 200 ms at a sample rate of 2 Hz.

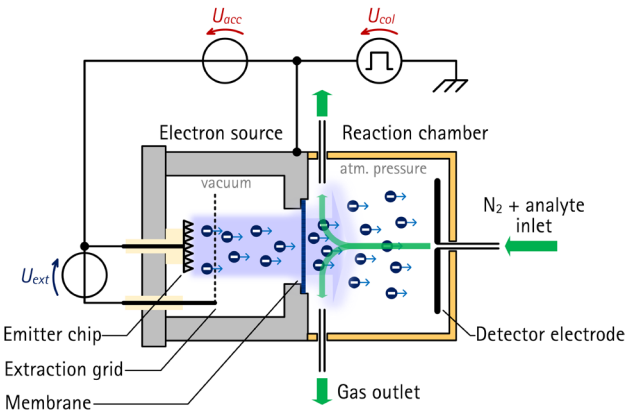

Fig. 3: Schematic of a pulsed non-radioactive ECD having an electron emitter based on field emission.

The sample gas is generated via permeation tubes in a precisely temperature-controlled permeation oven. The oven is purged with a constant gas flow controlled by a mass flow controller. An adjustable fraction of the analyte enriched gas is then mixed with the pure nitrogen carrier gas in a blender to generate a wide range of analyte concentrations [4]. The Sample gas flow through the ECD is controlled by a mass flow controller in line with a membrane pump positioned downstream of the ECD. 1,1,2-trichlorethane (CAS 79-00-5, purchased from Sigma Aldrich) is used as an analyte to characterize the ECD and to

compare it to the previously presented ECD with a thermionic electron source.

Results and Discussion

To determine the LoD of the ECD for 1,1,2-trichlorethane the source control electronics is set as follows, the acceleration voltage of the source is set to U_{acc}=3.5 kV, the extraction voltage limit to U_{ext}=600 V and the emission current setpoint to I_{emis}=30 nA. The ECD collector voltage is set to U_{col}=40 V, the pulse width to 5 µs and the detector current to 10 nA. This leads to a pulse frequency of about 5 kHz. The sample gas flow through the detector is set to 5 ml_s/min (mass flow at 20 °C and 1013.25 mbar). Using the above settings different analyte concentrations from 69 to 346 ppb_v have been measured, see Fig. 4. The slope of the resulting concentration to frequency curve is determined by linear interpolation. The LoD is defined as three times the standard deviation of the zero signal, here the measured noise of the frequency signal for pure nitrogen [4]. Due to the high instability of the field induced electron emission, the noise is significantly increased compared to our previously used thermionic electron emitter.

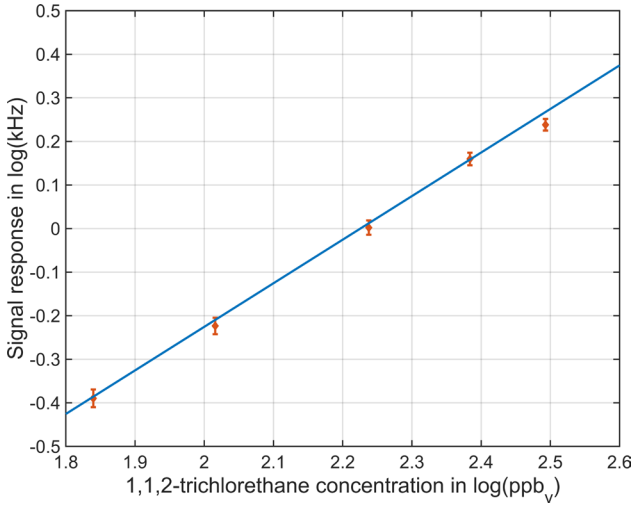

Fig. 4 Offset corrected logarithmic representation of the calibration curve. The solid line represents the linear correlation between the concentration and the pulse frequency.

The fluctuation of the field induced emission current is mainly caused by the stochastic nature of field emission, the wear of field emitter structures and a potentially unstable control circuit, which is additionally disturbed through electromagnetic interference caused by pulsing of the ECD. Thus, the resulting LoD for 1,1,2-trichlorethane is high as 21 ppb_v. However the LoD for 1,1,2-trichlorethane of the ECD equipped with our thermionic electron source is 2 ppb_v and thus over a decade lower [4]. Therefore, future research will concentrate on improving the field emission stability and the control circuit as already proposed in [19].

Conclusions

In this work we present preliminary results of a new field emission-based electron source coupled to our previously developed non-radioactive ECD [4]. Due to the high instability of the transmitted field emission current, the noise is significantly increased compared to our previously used thermionic electron emitter. This leads to a higher LoD for 1,1,2-trichlorethane of 21 ppb_v. Thus, the thermionic electron source based ECD having a LoD of just 2 ppb_v outperforms this new ECD by over a decade. This shortcoming is caused by an unstable emission current of the field emission based electron source, which is suspected to be a source control issue. To overcome this issue the source control electronics has to be improved to be able to precisely monitor and to control the emission current as shown in [19].

Acknowledgements

Supported by the German Federal Ministry of Economics and Technology (BMWi) upon decision of the German Bundestag, Grant ZF4249502GM8.

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