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Differential mobility spectrometers with tuneable separation voltage – Theoretical models and experimental findings

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ABSTRACT

Differential mobility spectrometry (DMS) is a method for identification of ions based on the nonlinear dependence of ion velocity on electric field intensity. The most important parameters characterising sensitivity and selectivity of DMS detectors are signal intensity, position of the peak in the DMS spectrum and the width of the peak. These parameters depend on the detector construction and on its control method. The shape and amplitude of the supplying (separation) voltage waveform are also very important. In this work, four different models of a DMS detector are studied. The models are based on simple algebra, partial differential equations, finite elements method and a statistical approach. All considered models give an opportunity for determining the key DMS parameters. Theoretical data are compared with the results of measurements performed with a detector of a simple structure for which tuning the parameters of separation voltage is possible.

1. Introduction

Differential mobility spectrometry (DMS) is an analytical method belonging to a wider group of techniques based on ion mobility spectrometry (IMS). This term refers to the principles, methods and instrumentation for characterising chemical substances on the basis of the velocity of gas-phase ions in an electric field [1]. The concept of the identification of ionic species by the measurement of their velocities in an electric field has been known for half a century [2]. The parameter characterising the kind of ions is the mobility coefficient (or simple mobility), K, i.e., the factor appearing in the dependence of velocity, v, on electric field intensity E. For weak electric fields the velocity of ions is proportional to the field intensity:

$$v = KE; \quad K = const \tag{1}$$

The obvious method for the determination of K is the measurement of drift time of ions through a defined distance in an electric field of known intensity. This method is used in IMS based on drift tubes (DT IMS). Equation (1) holds true for electric fields of slight intensities. For higher fields ($E > 5000$ V/cm), the mobility ceases to be constant [3]. As a result, the velocity of ions becomes a non-linear function of the electric field. The dependence of mobility on the electric field is usually described by Ref. [1]:

$$K = K_{LF}(1 + \alpha(E/N)) = K_{LF}\left(1 + \alpha_2\left(\frac{E}{N}\right)^2 + \alpha_4\left(\frac{E}{N}\right)^4 + \alpha_6\left(\frac{E}{N}\right)^6 + \ldots\right) \tag{2}$$

where K_{LF} is the value of mobility in a weak electric field, N is the number density of the gas, $\alpha(E/N)$ is the function describing the relationship between mobility and electric field, and $\alpha_2, \alpha_4, \ldots, \alpha_{2n}$ are series coefficients of the alpha function expansion. The proportion E/N is the measure of energy that can be transferred from the electric field to the ion. The unit of this quantity is 1 townsend (1 Td = 10^{-17} V cm^2).

DMS is a method in which the separation of ions is performed on the basis of non-linear $v = f(E)$ dependence [4,5]. A short and simple explanation of the operation principle of a planar DMS detector is

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given in the next section. A comprehensive description of the physical fundamentals and practical aspects of the DMS technique is contained in the monography of Shvartsburg [6]. The intensive development of the DMS method has led to the emergence of a large number of fundamental works [7–14], as well as research on possible applications [15–25]. The mechanical construction of DMS detectors is very simple, however, selection of their optimal features and the choosing of the proper working parameters is not trivial. For this reason, theoretical and practical optimisation of the parameters is performed [26–30].

The goal of our work is to optimise the operation parameters of a DMS device based on different methods for the description of the phenomena taking place in the detector. Such an approach can provide not only the possibility of predicting the detector features, but also allows to compare the models. It can be shown how accurate are particular methods of calculation and how significant are differences in results obtained using different models. The DMS detector used for the experiments was developed in such a way that changing the working parameters in a relatively wide range is easy to conduct. In particular, the tuning of separation voltage (SV) waveform gave the possibility of generating a series of results useful for testing theoretical descriptions of phenomena taking place in the detector.

2. Theoretical models of DMS detector

The prediction of detector properties can be made on the basis of considerations performed with different mathematical models. Four methods of calculation that allow us to determine important parameters, from an analytical point of view, are presented in the work. These methods use different mathematical approaches and their complexities are also very different. It is important to pay attention to the fact that models give only some approximation of the real parameters and certain features of the real system may not be taken into consideration.

The main part of the DMS detector is the separator. It is built from two electrodes separated by narrow gap. Two constructions of the separator are used in practice: planar (Fig. 1a) and coaxial (cylindrical) [31]. In planar separator the width of the gap d is usually less than 1 mm, the width w of the electrode is 5–8 mm and the length l is 15–25 mm. The electric field inside the separator is produced by the voltage consisting of an alternating part (SV) and a DC component named compensation voltage (CV). Next, considerations are limited to a planar detector for which the rectangular waveform of the voltage (Fig. 1b) is applied. The SV is the series of pulses of duration t_H and period T_{SV}. The proportion $x = t_H/T_{SV}$ is called the duty cycle. The amplitude (peak-to-peak) of the SV is equal to U_{SV} and its positive and negative parts are $U_H = (1-x)U_{SV}$ and $U_L = xU_{SV}$, respectively. The average value of such a defined waveform is equal to zero. The duty cycle is much less than 0.5. For this reason, the absolute value of the electric field intensity is higher for the positive part of the SV. Indexes H and L are used for the indication of voltage, the intensity of the electric field and the mobility for "high" and "low" parts of the waveform. The difference in field intensity for both parts of the waveform is the necessary condition for proper operation of the detector.

Ions are carried through the separator gap with flowing gas. An alternating field inside the gap causes the oscillating movement of ions (Fig. 1c). Despite that the average value of the SV is zero, the mean trajectories of the ions are not parallel to the separator plates. This results from differences in mobility at low and high intensities of the electric field. To allow the ions to pass through the separator, the tuned field created by CV of suitable value U_{CV0} has to be added to the alternating SV. The value of U_{CV0} is characteristic for a given kind of ion.

2.1. Simple model

2.1.1. "Equation of equal distances" and U_{CV0} calculations

For a given type of ions oscillating in the DMS separator gap, one value of compensation voltage U_{CV0} exists, for which the "average trajectory" of the ion is parallel to separator plates. This means that for the optimal value of CV, the distance passed by the ion during the part of the waveform period when the voltage is negative is equal to the distance for the time when the voltage is positive and the net displacement is zero. This statement constitutes the basis of the simplest model of DMS. The identity of both distances can be expressed by:

$$K_L(U_L - U_{CV0})(1-x)T_{SV}/d = K_H(U_H + U_{CV0})xT_{SV}/d \tag{3}$$

According to previous definitions of voltages and amplitudes:

$$U_L = U_H\frac{x}{1-x} \tag{4}$$

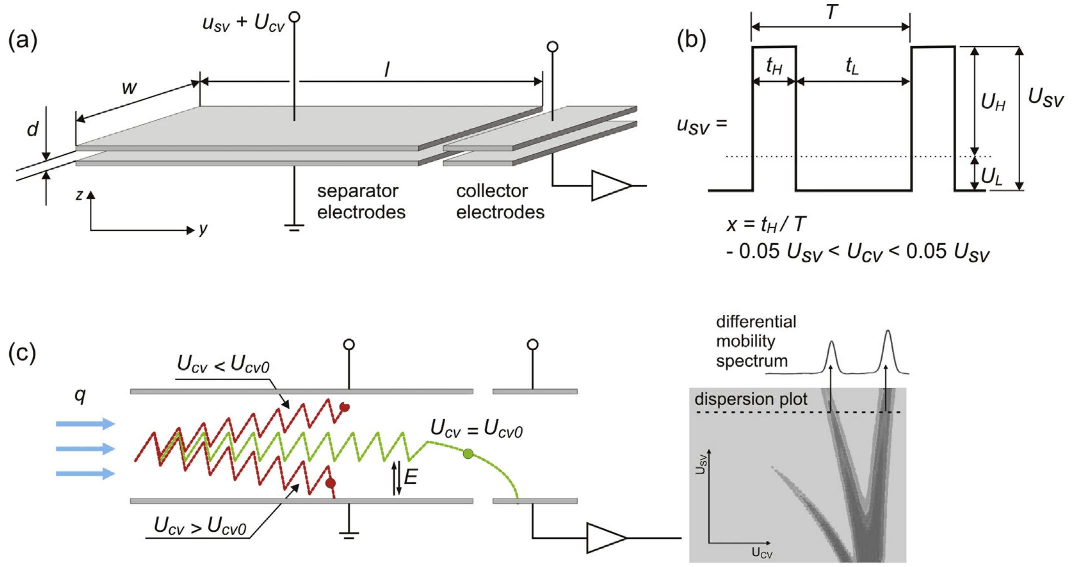

Fig. 1. Geometry of planar detector used in DMS (a), the shape of the SV waveform (b) and the principle of detectors' operation (c).