

ELECTRICAL AEROSOL SPECTROMETER OF TARTU UNIVERSITY

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Abstract

The electrical aerosol spectrometer of parallel measuring principle at Tartu University is an efficient instrument for rapid measurement of the unstable size spectrum of aerosol particles. The measuring range from 10 nm to 10 μm is achieved by using simultaneously a pair of differential mobility analyzers with two different particle chargers. The particle spectrum is calculated and measurement errors are estimated in real time by using a least-squares method. Experimental calibration ensures reliability of measurement. The instrument is well suited for continuous monitoring of atmospheric aerosol.

INTRODUCTION

We study compact particles characterized by scalar size. The size is expressed by the diameter or by some equivalent diameter if the particles are non-spherical. Particle size distribution or size spectrum is a fundamental characteristic of an aerosol allowing for easy calculation of common integral parameters such as the particle number concentration, volume concentration, particle's mean diameter, etc.

Measurement of the size spectrum of fine particles is complicated and expensive. Atmospheric aerosols of size ranging from nanometers to tens of micrometers are usually measured with several spectrometers of different working principles. Linking of the results obtained by different instruments is often a source of serious problems. When the size fractions are measured sequentially, concentration fluctuations of atmospheric aerosol can cause significant dynamic errors in the shape of the spectrum.

The electrical method of aerosol spectrometry proposed by Rohmann (1923) and developed by the Minnesota school (Whitby and Clark, 1966) is acknowledged as one of the best and most widely applied methods for measurement of submicrometer aerosols. Physicists at Tartu University have proposed a method involving two simultaneously operating chargers and a parallel measurement principle, and have developed an original wide-range electrical aerosol spectrometer (EAS) (Tammet et al., 1973; Tamm, 1975; Tammet, 1975, 1980, 1983, 1992; Mirme et al., 1981; Mirme, 1982, 1983, 1984, 1987, 1988; Mirme and Peil, 1983; Noppel, 1983, 1985; Tammet et al., 1983; Mirme et al., 1984; Kikas et al., 1985; Mirme and Tamm, 1991; Tammet and Noppel, 1992; Mirme, 1994; Kikas et al., 1996).

PRINCIPLES OF OPERATION

The spectrometer consists of two physically independent compartments. In each compartment the particles pass a unipolar charging unit and a second order differential mobility analyzer. One charging unit uses a weak field ion diffusion mechanism (diffusion charging); the other uses a strong field ion impact mechanism (field charging). The association of different charging mechanisms makes a wide size range possible. The size-mobility relation for the two mechanisms, for charging conditions applied in the EAS, is illustrated in Fig. 1. Field charging provides high sensitivity and resolution in supermicron size range, it was used by Rohmann (1923), and by Langer and Radnik (1961). Diffusion charging provides good resolution in submicron size range, it was used by Whitby and Clark (1966). Both methods have a serious disadvantage: the conversion from mobility to size is ambiguous. The Electrical Aerosol Spectrometer of Tartu University is a parallel multichannel instrument with many electrometric amplifiers simultaneously measuring the electric currents carried by particles of different mobility fractions. It is not a simple composition of two instruments using two different methods

of particle charging. The ambiguity of one charging method can be corrected using measurements by a different method because the weights of sub- and supermicron particles are essentially different in responses to different charging methods in the EAS. Actually, the methods are linked by means of an unitary least-square model which considers all measuring channels of both compartments on equal rights.

The immediate physical output of the EAS is a set of electrometer signals $\mathbf{y} = \{y_1 \dots y_m\}$ where the signals from the two compartments are merged and considered as a unitary vector. The task is to

evaluate the particle size spectrum $f(d)$ defined in such a way that $\int_{d_1}^{d_2} f(d)dd$ is equal to the

number concentration of particles of size in the diameter range of (d_1, d_2) . The problem is solved using the mathematical model of the physical measurement unit as an equation and the measured value of the vector \mathbf{y} as a data. The information transformation is described by the chain $f(d) \rightarrow f(k) \rightarrow \mathbf{y} \rightarrow f^*(d)$, where k is the particle's electrical mobility, $f(k)$ is the mobility spectrum, and $f^*(d)$ is the desired estimate of the size spectrum. The difference $f^*(d) - f(d)$ is the final measurement error.

The transformation of information $f(d) \rightarrow \mathbf{y}$ is described by the mathematical model of the spectrometer. If the spectrometer satisfies the principle of superposition of component spectra, then the transformation is linear:

$$y_j = \int h_j(d)f(d)dd + u_j, \quad j = 1 \dots m. \quad (1)$$

Information about the instrument is expressed by functions $h_j(d)$ called the apparatus functions. The addend u_j is the immediate measurement error, or apparatus noise, characterized by the covariation matrix $\mathbf{D} = \langle u_i u_j \rangle$. Being given the system of m equations (1), up to m scalar values can be determined by means of an accurate mathematical procedure. Hence the spectrum could be presented by a finite set of numbers $\mathbf{f} = \{f_1 \dots f_n\}$ where $n \leq m$. A linear model

$$f(d) = \sum_{i=1}^n f_i f^i(d), \quad (2)$$

with predetermined co-ordinate spectra $f^1(d), f^2(d), \dots, f^n(d)$ is well suited for our purpose.

Tammet (1980) proposed narrow triangle co-ordinate functions on a scale of $1/d$ resulting in a piecewise linear model of the particle size spectrum. Combination of Equations (1) and (2) leads to a system of algebraic equations

$$y_j = \sum_{i=1}^n H_{ji} f_i + u_j, \quad j = 1 \dots m \quad (3)$$

which can be expressed in matrix form as

$$\mathbf{y} = \mathbf{H}\mathbf{f} + \mathbf{u} \quad (4)$$

and called the spectrometer apparatus equation. \mathbf{H} is called the apparatus matrix. The matrix elements are

$$H_{ji} = \int h_j(d)f^i(d)dd. \quad (5)$$

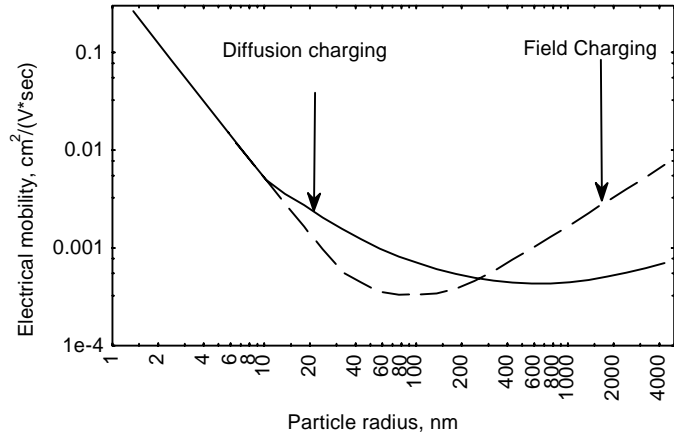


Fig. 1. Dependence of the charged particle electrical mobility on particle radius for weak field (diffusion) and strong field charging mechanisms for charging parameters used in the EAS.

The apparatus equation (4) can be solved and the estimate $f^*(d)$ of the size spectrum can be obtained by the Gauss-Markoff least-square method.

SINGLE-CHANNEL AND MULTI-CHANNEL METHODS

In a single-channel spectrometer the values y_i are measured sequentially in time at different values of a certain control parameter (usually voltage on a mobility analyzer). The method has been applied in well-known spectrometers of TSI and Hauke. A single-channel spectrometer contains only a single particle detector, such as an electrometer (Whitby and Clark, 1966) or a condensation particle counter (Knutson and Whitby, 1975; Wang and Flagan, 1989).

The multi-channel method developed at Tartu University uses a multi-electrode particle collecting system either with a set of electrometers (Mirme et al, 1981; Tammet et al., 1983; Mirme et al., 1984) or with one electrometer and an electrometric commutator (Tammet et al., 1973). The first alternative is preferred as the more reliable. Although the instrument is technically more complex, it has a number of advantages:

1. A representative average spectrum over the measurement period is obtained even for spatially nonhomogeneous and fluctuating aerosols. Dynamic measurement errors are avoided and statistical characteristics of rapid aerosol variations can be provided.

2. Information is collected m times quicker when compared with a single-channel instrument. Rapid changes of aerosol spectrum shape and concentration can be measured.

3. Precipitated particles can be measured by electron microscope separately for each channel and a reliable experimental calibration of the spectrometer is possible. The chemical composition of the particles of specified size fractions can be studied.

A large number of electrometric amplifiers seems to be a disadvantage of the method, not only because of manufacturing expenses but also because of the enhanced probability of insulation failures. This disadvantage is essentially suppressed in the EAS by use of the sophisticated version of the least-square method and by redundancy of the primary measuring information. The noise of each electrometer is continuously monitored during the measuring process. The estimated mean-square value of the noise is considered as the reciprocal weight of every individual channel signal in the equations of the least-square method. Thus the effect of channels with bad electrometric insulation is strongly suppressed in the result presented in terms of size distribution. The number of measured signals exceeds the number of size fractions in EAS by a factor of two. Due to the redundancy of electrometric channels an individual channel can fail without a major effect on the results because the neighboring channels overlap on the mobility scale.

TECHNICAL DESCRIPTION

The design of the EAS is presented in Fig. 2. High sensitivity and resolving power have been reached by unipolar charging of particles. Particles up to the diameter of $0.5 \mu\text{m}$ are resolved using unipolar ion diffusion charging. Particles of diameter over $0.3 \mu\text{m}$ are resolved using unipolar charging in a strong electric field. The EAS contains two identical mobility analyzers, one provided with a diffusion charger (D-analyzer), and the other with a strong field charger (E-analyzer).

The collecting electrodes of both axisymmetric mobility analyzers are split into sections dividing the entire measurement range nearly homogeneously on a logarithmic scale of particle size. There are 26 sections provided with electrometric amplifiers, so the number of channel signals m is 26. The number of spectrum fractions n is software selectable. If we have four fractions per size decade (twelve fractions in total), there are two channels per fraction. The redundancy sustains the working capacity of the instrument, should any of the individual measuring channels fail.

The air passing through the analyzers consists of three coaxial sheaths. The outer sheath is clean, filtered by an electric filter. The intermediate sheath carries the charged particles into the

analyzer. The air flowing in the inner sheath is removed and it does not participate in the measurement process. Thus the particles generated by the corona discharge in the charger (Tamm et al., 1992) are eliminated and they do not affect measurements. Total inlet flow rate is $800 \text{ cm}^3/\text{s}$, being $200 \text{ cm}^3/\text{s}$ for the inner and intermediate sheaths of each of the two analyzers. Flow rate of the filtered outer sheath air is $600 \text{ cm}^3/\text{s}$.

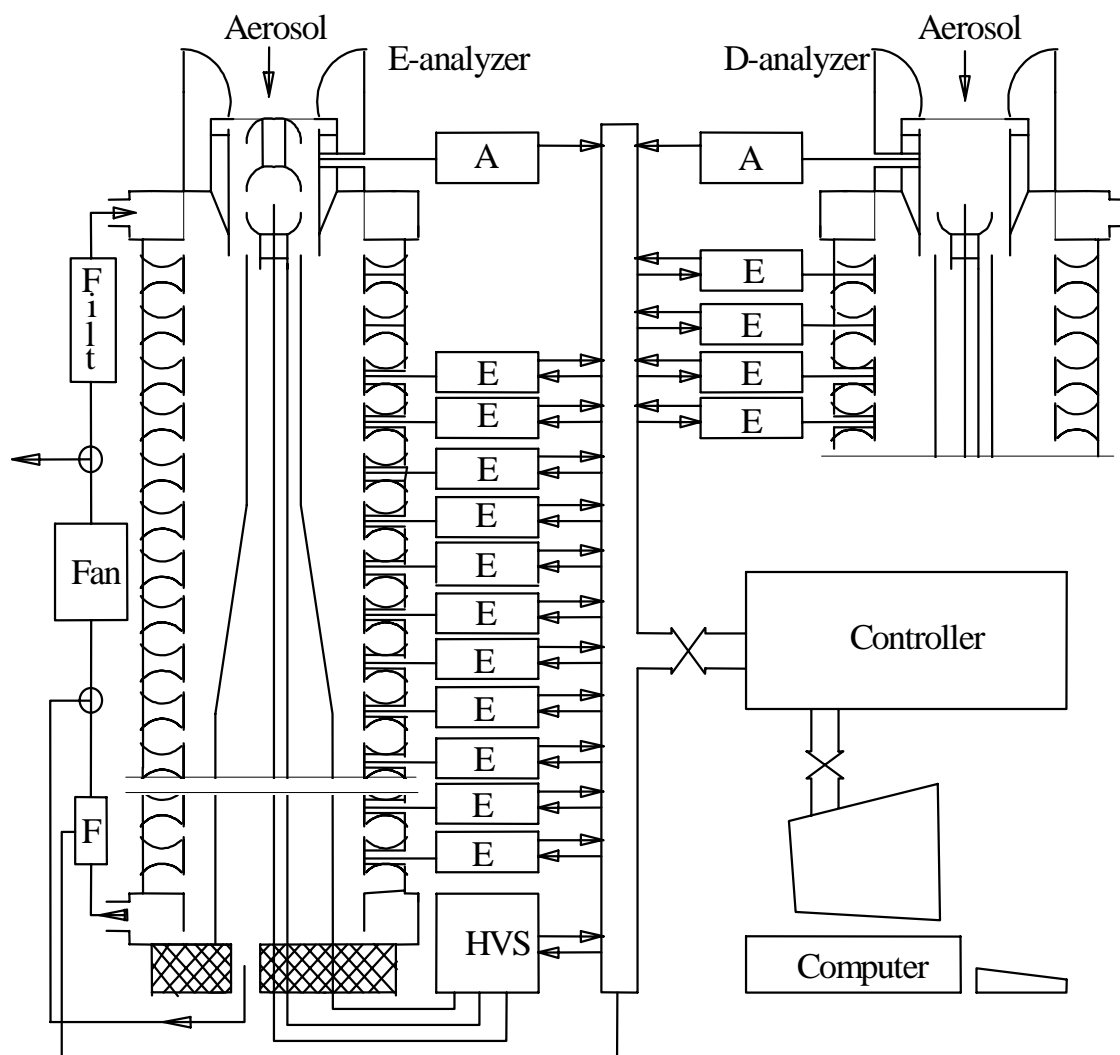


Fig. 2. Design of the spectrometer. A - corona current amplifiers, E - electrometric amplifiers, VS - voltage supply, F - flow sensor.

To minimize the effects of leakage currents and the offset drift of the electrometric amplifiers, the polarities of the chargers are periodically changed while the voltage polarity on the measuring condenser remains unaltered. The offset level and noise of the amplifier output signals are recorded by reversing the polarity of particle charges. A measurement cycle consists of measurements at both polarities of particle charges.

A computer via a controller of special design controls the instrument. Aerosol takes about one second to pass an analyzer. The channel currents are recorded synchronously with the movement of aerosol through the analyzer. The noise of the electrometric amplifiers is about $2.5 \times 10^{-16} \text{ A}$. Charging parameters are stabilized by feedback circuits. Corona currents, voltages on the analyzers and air flow rates are measured and recorded for every measurement cycle.

Voltage on the analyzers is 800 V . The measurement range of the spectrometer can be modified by changing the voltage on the D-analyzer. At 43 V the minimum diameter of measured particles is 2.4 nm .

Linear dimensions of the instrument are 440×490×900 mm, mass 70 kg.

DATA PROCESSING AND INSTRUMENT CALIBRATION

The particle size spectrum is estimated immediately after every measurement cycle. At first, the raw data \mathbf{y} is pre-processed: static and dynamic errors of the electrometric amplifiers are numerically corrected, and the offset level is subtracted. When commencing a measurement, the covariation matrix of immediate measurement errors \mathbf{D} is estimated on the basis of experience with former measurements. Afterwards, matrix \mathbf{D} is iteratively adjusted using the data on variation of the offset level. For every measurement cycle the covariation matrix of the particle size spectrum \mathbf{f} is calculated: $\mathbf{C}=(\mathbf{H}^T\mathbf{D}^{-1}\mathbf{H})^{-1}$. The standard deviations of the spectrum elements are the square roots of the diagonal elements of matrix \mathbf{C} . The least square estimate of the spectrum is calculated:

$$\mathbf{f} = \mathbf{C} \mathbf{H}^T \mathbf{D}^{-1} \mathbf{y} . \quad (6)$$

Finally, the spectrum is expressed in accordance with Eq. 2, and all the required parameters of the aerosol (fraction concentrations, total concentration, mean diameters, etc.) can be calculated.

The calibration of the spectrometer here actually means the determination of the apparatus matrix \mathbf{H} . Several ways of calibration have been proposed: a theoretical method (Tammet et al., 1983), a method of monodisperse well defined aerosols (Kikas et al., 1985), a method of microscopic analysis of the deposited particles (Tammet, 1983), a parametric method and a combined method (Tammet and Noppel, 1992), as well as a direct method using aerosols of well known spectra (Mirme, 1987).

The parametric method and the direct method have been used so far. The direct method provides the more reliable results. Use has been made of a set of well-defined aerosols generated by electrical separation and a vibrating orifice generator was used. For each test aerosol with known spectrum \mathbf{f} , the vector \mathbf{y} of the spectrometer signals has been recorded. The next step is construction of the generalized apparatus equation

$$\mathbf{Y} = \mathbf{H} \mathbf{F} \quad (7)$$

in which the vectors \mathbf{y} and \mathbf{f} are the columns of the matrices \mathbf{Y} and \mathbf{F} . After transposing the equation (7), it can be split into m equations of type (4), where the spectra vectors are replaced by the rows of matrix \mathbf{H} . The elements of \mathbf{H} are determined by solving these equations. Last, the random errors of the matrix elements have been suppressed by using minimum smoothing of the columns and rows according to a semiempirical parametric method.

MAIN TECHNICAL DATA AND LIMITATIONS

The basic measuring range of the instrument according to the particle diameter is from 10 nm to 10 μm . As an alternative, the complementary range from 2.4 nm to 18 nm is physically available. The experimental calibration of the instrument has been performed only in the basic measuring range today. The number of the spectrum fractions in output information is software controlled. As a standard, twelve fractions are resolved at the basic measurement range (4 per decade of d). Fraction boundaries are as follows in nanometers: 10, 18, 32, 56, 100, 180, 320, 560, 1000, 1800, 3200, 5600, 10000.

The measurement range according to the particle concentration is limited by sensitivity and dynamic range of the electrometers and by performance of the chargers, and depends on the particle size. For particles of diameter 10 nm, 100 nm, 1 μm and 10 μm the measuring ranges are $(1 \times 10^2 - 1 \times 10^5)$, $(1 \times 10^1 - 2 \times 10^4)$, $(3 \times 10^{-1} - 1 \times 10^3)$ and $(2 \times 10^{-2} - 5 \times 10^1)$ particles per cm^3 , respectively.

The duration of one measurement cycle is software controlled and can be set from 4 sec to several tens of minutes. Aerosol of high concentration can be measured in a very short time

interval while at low concentrations the sensitivity and signal-to-noise ratio is improved by lengthening the measurement time.

Having a wide size range, the EAS is not of very high resolving power, which can be a problem when measuring the quasimonodisperse aerosols. A possible source of errors may be the dielectric constant of the particle matter, which can influence the charge and mobility of the bigger particles. The standard calibration of the EAS is performed for conductive particles common in the atmospheric air. The concentration of nonconducting dielectric particles of $d > 0.3 \mu\text{m}$ will be underestimated when using the standard calibration.

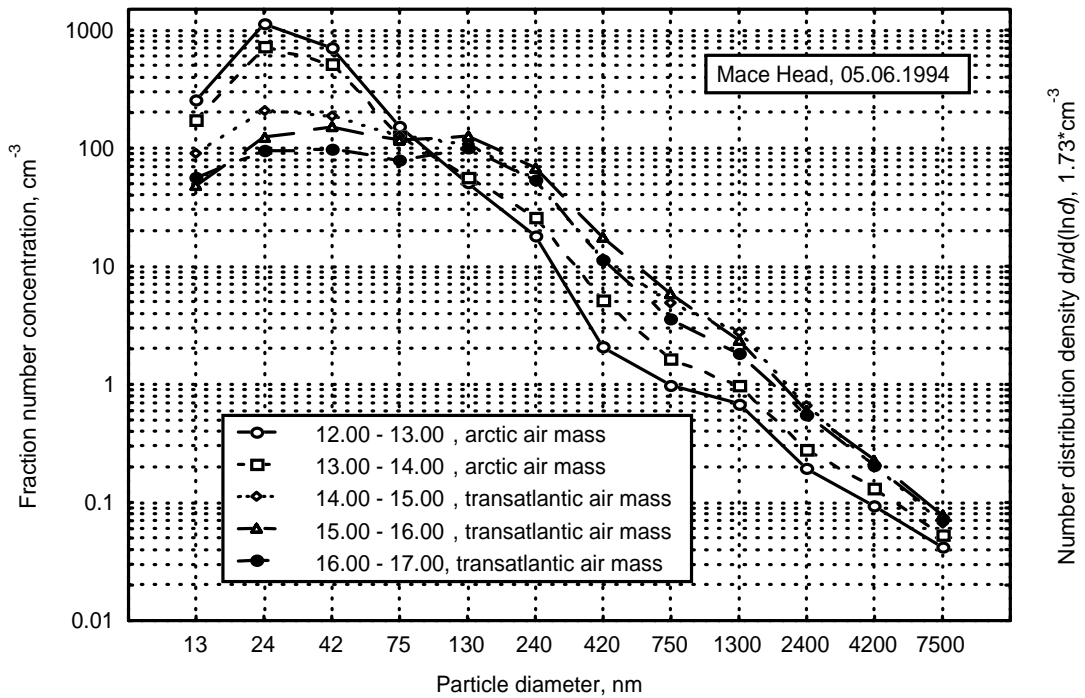


Fig. 3. Hourly mean atmospheric aerosol spectra measured by the EAS in Mace Head, Ireland, during a three-month measuring campaign in spring and summer, 1994.

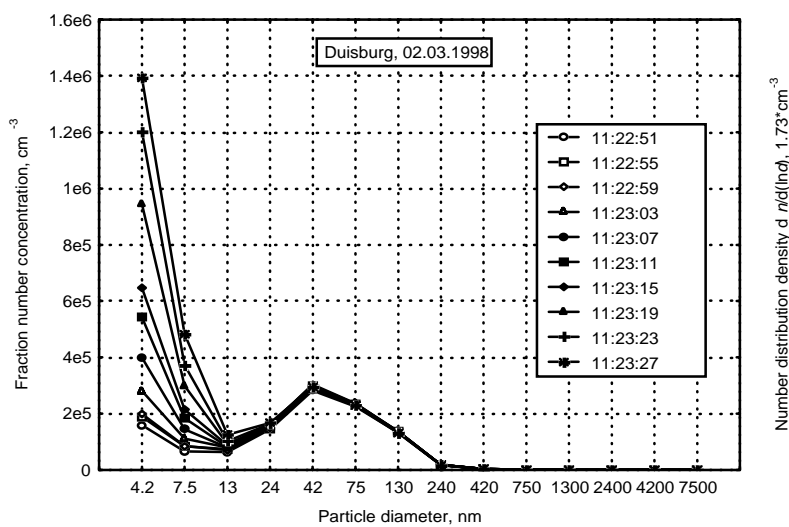


Fig. 4. Four-second mean spectra of aerosol generated by alcohol fire, measured by modified EAS in the fire detection laboratory of the Department of Communication Engineering at the Gerhard-Mercator-University in Duisburg, Germany.

MAIN APPLICATIONS

The EAS is specially designed for continuous monitoring of atmospheric aerosol. About 60,000 spectra have been recorded during the 21 measurement campaigns so far. The EAS can be used for the study of rapid changes of aerosol spectra in nucleation research and combustion research, for quick filter testing with polydisperse test aerosols and for many other purposes.

Fig. 3 depicts an example of hourly mean atmospheric aerosol spectra measured by the EAS. The hourly means are obtained by averaging of six directly measured 10-minute mean spectra. Effect of the rapid change of air mass is clearly seen. Fig. 4 shows the high time resolution of the EAS. Four-second mean spectra were measured in the fire detection laboratory of the Department of Communication Engineering at the Gerhard-Mercator-University in Duisburg, Germany, for a quickly developing aerosol generated by alcohol fire. The latter measurements were performed by a new version of the EAS with extended measuring range from 3.2 nm to 10 μm . In Figs 3 and 4, the geometric mean diameters of the particles in the above-mentioned standard size fractions are shown on the *d*-axis.

ACKNOWLEDGEMENTS

We wish to thank our colleagues from the Air Electricity Laboratory of the Department of Environmental Physics of Tartu University, especially Ülle Kikas, Toomas Bernotas, and Aivo Reinart for discussion of the problems and technical support. The research was supported in part by the Estonian Science Foundation grant no. 616.

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