

3. INSTRUMENTATION AND DATA PROCESSING

3.1. General layout of the system

A complex of air ion spectrometers covering a mobility range of $0.00041\text{--}3.14\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was installed at Tahkuse in 1988 [Tamm et al., 1990; Hörrak et al., 1990, 1994]. The upper mobility limit was chosen to collect the smallest existing air ions. The lower mobility limit is determined by the technical parameters of the equipment. The complex consists of three original multichannel aspiration spectrometers [Tamm et al., 1970]. In addition to the air ion mobility spectrum the system is able to measure and record basic meteorological parameters, and NO_2 concentration. A diagram of the instrumentation is presented in Figure 7.

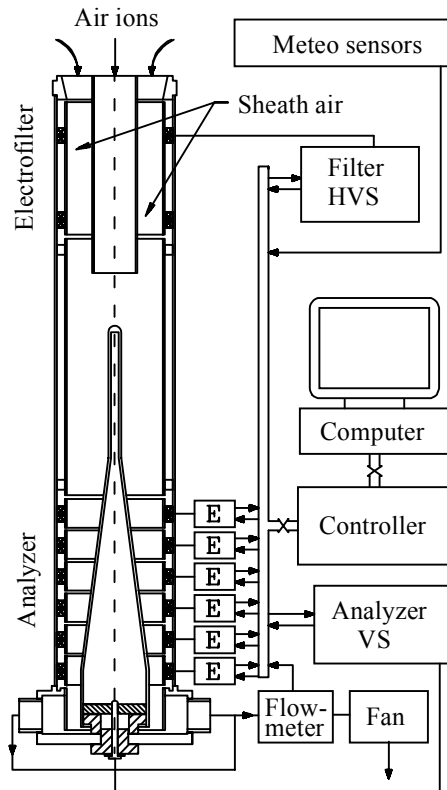


Figure 7. Small air ion spectrometer IS_1 and the measuring system. E is electrometer, HVS is high voltage supply and VS is voltage supply. External dimensions of the spectrometer: height 695 mm, diameter 122 mm.

The air ion mobilities are measured by a small air ion spectrometer (IS_1), an intermediate ion (IS_2) and a large ion spectrometer (IS_3). Direct voltage for each spectrometer is provided by the high-stability voltage supply controlled by the controller. Besides the control of the components of the system, the controller is responsible for the reception and transmission of signals. A computer program controls the measurement, preliminary data processing and storage. The spectrometers are in the same air tract with a common fan. As a precaution against possible power failures the computer, the controller, and the voltage supply have an uninterrupted power supply. The above devices are enclosed in a thermally insulated stable-climate chamber, which makes it possible to use the equipment throughout all four seasons. The chamber and the tube of the air channel are electrically earthed.

The data acquisition system was gradually developed and twice (1992 and 1995) reconstructed. The controller used in the present system resembles the device described in [Mirme, 1982]. The structure of air ion mobility spectra measurements and primary data processing is similar to that published in papers [Tamm et al., 1987a, Tamm et al., 1990].

The mobility spectra of positive and negative air ions were measured every 5 minutes. The hourly averages and standard deviations of air ion fraction concentration (i.e. more exactly the number of elementary charges per cm^3) inside the hourly periods were recorded together with the values of the meteorological parameters, and the concentration of NO_2 .

3.2. Air tract

The air is sucked into the mobility spectrometers through an opening in the south gable of the building at a height of about 5 m from the ground (Figure 8). A metal shelter provides protection against precipitation. To prevent the effect of wind to the airflow, the air inlet (above) and outlet (beneath the inlet) have been placed in the same gable with a space of about 1 m. The length of an aluminum tube that conducts the air sample to the spectrometers is about 2 m, with a cross-section of $13 \times 21\text{ cm}^2$. There are thin longitudinal metal sheets in the tube for the suppression of turbulence. The channel grows narrower in the direction of the flow. A metal grid (with mesh about $3 \times 3\text{ mm}$) in the inlet and outlet provides protection against flying objects (hair, insects, fuzz). The total air flow rate is about 16 liters per second, and air speed about 0.6 m s^{-1} . The time of air travel in the channel is about 3 s.

The airflow is created by a sucking fan feed on the ferro-resonance stabilizer. A collector chamber at the inlet end of the fan provides calibrated airflow through the spectrometers. The systematic uncertainty of the flow rate is estimated $\pm 2\%$; the random component of about 80 s averages is less than 0.5%.



Figure 8. The input and output of the air tract (left) and a thermally insulated stable-climate chamber (right).

3.3. Air ion spectrometers

The air ion spectrometers have been designed and built at the Institute of Environmental Physics of the University of Tartu. According to the principle of second-order differential mobility analyzer (DMA) [Tammets, 1970], the measuring condensers have a divided airflow at the entrance of the measuring condenser and multiple collector electrodes. All three measuring condensers have a coaxial shape (Figures 7 and 9). At the entrance of each measuring condenser, the incoming airflow is divided into two parts by a preliminary condenser (electrofilter). The outer coaxial layer is deionized (sheath air), while the central flow passes through, retaining its natural condition. Behind the preliminary condenser, the measuring condenser has one inner electrode and multiple outer electrodes. Naturally charged particles (cluster ions and aerosol ions) carried by air flow drift in the radial electric field and are deposited on different electrodes of the mobility analyzer according to their mobilities. The electric current of ions through the collector electrodes is measured by electrometrical amplifiers. Each collector electrode has individual electrometrical amplifier.

The apparatus function or transfer function of a channel signal according to the mobility has the approximately triangular or trapeze shape smoothed a little by the diffusion of air ions [Tammets, 1970].

The measuring condenser of the small air ion spectrometer (IS₁) presented in Figure 7 is identical to the one described in [Tammets et al., 1987a]. The IS₁ has six collector electrodes. To ensure efficiency of the preliminary condenser (electrofilter), the respective polarity and value of the voltage were chosen. The central electrode is grounded, and the DC voltage is applied to the outer electrode. The polarity of the voltage is the same as on the central electrode of

the measuring condenser. The technical parameters of the spectrometer IS₁ are presented in Table 1. The limiting mobility of the preliminary condenser is about four times lower than the minimum limiting mobility of the measuring condenser. The Reynolds number (Re) in the inlet of the spectrometer (electrofilter) is close to the critical value of about 1100. A metal honeycomb (thin metal sheets with mesh 11×8 mm and height 80 mm) with Re of about 200 was added in the inlet of the spectrometer for the suppression of turbulence.

The basic characteristics of the intermediate and large ion spectrometer (IS₂ and IS₃) are identical to those published in [Salm, 1981]. The only significant modification is that preliminary condensers have been added to the entrances of the measuring condensers (Figure 9); those give the spectrometer the characteristics of a differential spectrometer of the second order. One of the two identical preliminary condensers is depicted in Figure 9. Electrodes 15 and 17 are grounded, electrode 16 is given DC voltage. The air between electrodes 15–16 and 16–17 is deionized and serves as sheath air, whereas the air passing through electrode 15 retains its natural condition. The voltage applied to the electrode 16 is of opposite polarity to that on the measuring condenser.

The intermediate and large ion spectrometer has two measuring condensers: IS₂ for small and intermediate ions and IS₃ for large ions (Figure 9). It has ten collector electrodes. The first channel of condenser IS₂ has integral characteristic, while the other channels are differential with the approximately triangular or trapeze apparatus functions. The limiting mobilities of the preliminary condensers are about 8 and 4 times smaller than the respective minimum limiting mobilities of the mobility analyzers of IS₂ and IS₃.

The Reynolds number for the sheath air of the preliminary condenser of IS₂ is about four times less than the critical, but the Reynolds number of the air passing through the central part is nearly equal with the critical value (about 1100). The respective Reynolds numbers for the pre-condenser of IS₃ are about four times less compared with IS₂. A metal grid (with mesh of 2×2 mm) in the inlet of spectrometer IS₃ provides protection against flying hair and insects.

Table 1. Technical parameters of spectrometers IS₁, IS₂ and IS₃.

Spectro- meter	Airflow, cm ³ s ⁻¹		DC voltage, V		Limiting mobilities, cm ² V ⁻¹ s ⁻¹
	Total	Sheath air	Preliminary condenser	Measuring condenser	
IS ₁	9800	8140	860	47.5	0.8 – 3.14
				150	0.25 – 1.0
IS ₂	4840	2500	900	406	0.29 – ∞
					0.016 – 0.29
IS ₃	1200	620	1800	890	0.00041 – 0.021

The spectrometers are heated (with the power of 45 W for IS₁ and 75 W for IS₂+IS₃) about by 5–10°C over the temperature of ambient air. This measure prevents the condensation of water vapor on insulators, reducing a leakage current, and assures reliable measurements in the conditions of high humidity.

According to the measurement principle, the extremely stable voltage (instability less than 1 mV) on the measuring condenser is necessary to measure the current of about 1–100 fA carried by air ions. The ratio of signal to noise was improved by using electrometric amplifiers with the time factor of about 50 s. The electrometric amplifiers used in spectrometers have a field-effect-transistor (MOSFET) in the inlet, a sensitivity of about 0.1–1 fA and noise less than 0.25 fA [Miller, 1981]. The feedback circuit of the amplifier consists of parallel resistor (1 TΩ) and condenser (50 pF).

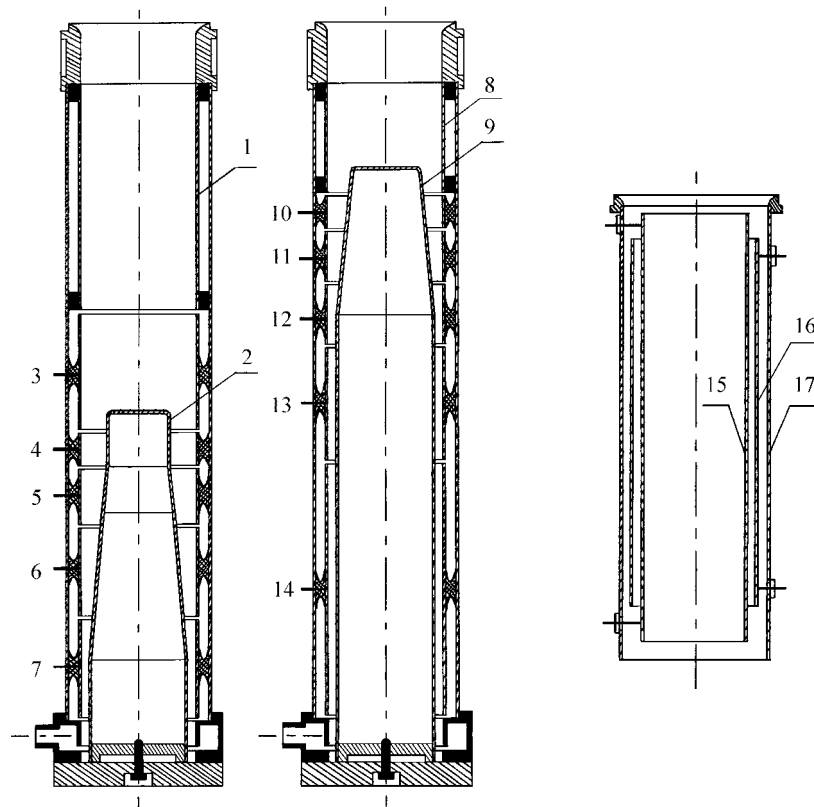


Figure 9. Measuring condensers of small and intermediate ions IS₂ (left) and large ions IS₃ (center), and the preliminary condenser (right). 1 and 8 are grounded inlets, 2 and 9 are central electrodes, 3–7 and 10–14 are the outputs of collector electrodes, 15–17 are the electrodes of pre-condenser. External dimensions of the measuring condensers: height 648 mm, diameter 122 mm, and pre-condenser: height 390 mm, diameter 126 mm.

The state of air ion spectrometers is inspected by a special diagnostics procedure [Tammets, 1990], as a rule, once a month. The parameters of the electrometric amplifiers (measuring resistance and capacitance) are verified, the current technical condition of the insulators, as well as the rate of the radioactive contamination of the measuring capacitors is determined.

3.4. Sensors

According to their function, the sensors of the measuring system can be divided into two groups: the sensors of meteorological parameters and air pollution (NO₂), and the sensors monitoring the technical parameters of the measuring system itself. The first group comprises the sensors of:

- 1) wind speed and wind direction (anemometer M63M-1 with a supplementary device for electrical output, the measuring range is 1–60 m s⁻¹ (accuracy ±0.5 m s⁻¹) and 0–360° (accuracy ±10°), respectively [Sternzat, 1978]);
- 2) the temperature of the air (calibrated temperature-sensitive resistor MMT-4, the measuring range ±40 C, accuracy of about ±1°C);
- 3) relative humidity and temperature of the air (HMP 130Y and Pt-100, production of Vaisala, relative humidity 0...100% (accuracy 2–3%) and temperature –20...+60 (accuracy ±0.2°C));
- 4) atmospheric pressure (a unified sensor of pressure, system KRAMS, 570–1090 mb, accuracy ±0.2 mb [Sternzat, 1978]);
- 5) sensor of NO₂ (original design of the University of Turku, Saltzman method, detection limit 0.5 ppb (1μg m⁻³), accuracy ±0.1 ppb (0.2 μg m⁻³) [Punkkinen, 1988]).

The sensor of the wind direction and speed has been installed about 120 m south from the building, on a flat open grassland, on a mast at a height of about 12 m. The sensor of the air temperature is situated near the inlet of the main air tract. The sensor of the relative humidity and air temperature HMP 130Y has been installed about 10 m south from the observatory building at a height of about 2 m above the ground (under the eaves of a small stand). The sensor of atmospheric pressure has been installed in the thermal-insulation chamber. The sampling inlet of NO₂ sensor has been mounted under the eaves of the building at a height of about 3 m above the ground, on the eastern side of the building.

The sensors monitoring the technical parameters of the system comprise of the sensor of the mains voltage, and the sensor of temperature in the thermal-insulation chamber (graduated temperature-sensitive resistor MMT-4, a component of the temperature regulating system).

3.5. Electrical aerosol spectrometer

The Electrical Aerosol Spectrometer (EAS) was applied during an extensive study of atmospheric air ion parameters conducted at Tahkuse in April and May, 1994. The EAS is a multichannel aerosol spectrometer designed and built at the Institute of Environmental Physics of the University of Tartu and described in papers [Mirme, 1994; Kikas *et al.*, 1996, Tammet *et al.*, 1998].

The EAS measures the size distribution of particle concentration in a diameter range of 10 nm–10 μm. The spectrum is logarithmically distributed into 12 fractions. The EAS contains two identical mobility analyzers: one provided with a diffusion charger, and the other with a strong electric field charger. High sensitivity is reached by unipolar charging of particles and a high inlet flow rate (200 cm³s⁻¹ per analyzer). Particles up to a diameter of 0.5 μm are resolved using unipolar ion diffusion charging. The particles of a diameter of above 0.3 μm are resolved using unipolar charging in a strong electric field. Although unipolar particle charging and mobility classification are used in the EAS, the data inversion in it is based on experimental calibration by means of standard aerosols [Kikas *et al.*, 1985; Mirme, 1987; Tammet and Noppel, 1992].

The estimated errors of the fraction number concentrations have the values of 25, 3, 0.1 0.004 particles per cm³ for size fractions at 10 nm, 100 nm, 1 μm, and 10 μm, respectively. The EAS has been compared with the electrical aerosol analyzer (TSI model 3030) [Mirme *et al.*, 1987], with instruments for measuring particle total number concentration during a workshop in Vienna in June, 1993, and with the aerosol mobility analyzers (SMPS/DMPS) in Petten, 1997 [Khlystov *et al.*, 2001].

3.6. Estimation of the air ion fraction concentrations

The response of air ion mobility spectrometer to the charge density spectrum of air ions is given by equation [Tammet, 1970]

$$P(k_j) = \int_k G_p(k_j, k) \rho(k) dk, \quad (5)$$

where $G_p(k_j, k)$ is the apparatus function for charge density spectrum $\rho(k)$ and $P(k_j)$ is the record of spectrometer; k is the mobility of an ion, and k_j is the limiting mobility characteristic for j collector electrode of the measuring condenser. $P(k_j) = J/(e\Phi)$, where J is an electric current, carried by ions through the collector electrode and recorded by means of an electrometric amplifier; e is the elementary charge; and Φ is the rate of airflow passing through the central electrode of the preliminary condenser. The ideal apparatus functions of the second order differential mobility analyzer (as an example for the first three

channels of IS₁) are presented in Figure 10. The real apparatus functions are smoothed a little by the diffusion of air ions.

In general, the records of the set of mobility spectrometers (IS₁, IS₂ and IS₃) can be presented by a matrix equation [Tammet, 1975b, 1980]

$$P = G_p \rho + \Delta P, \quad (6)$$

where P is the apparatus record (vector of 21 output signals of the logical channels of spectrometers); ΔP is the vector of output signal errors (21 logical channels); G_p is the apparatus matrix (21×20 elements), and ρ is the vector of spectrum (20 elements). The apparatus equation (Eq. 6) can be solved using the least squares method of Gauss-Markoff [Tammet, 1975b]:

$$\rho = (G^T D^{-1} G)^{-1} G^T D^{-1} P, \quad (7)$$

where D is the covariation matrix of the apparatus vector (21 × 21 elements). The errors of the estimated components of the spectrum vector are given by the diagonal elements of the covariation matrix of the spectrum $(G^T D^{-1} G)^{-1}$. The superscript T denotes the transposed matrix and "−1" the reciprocal matrix.

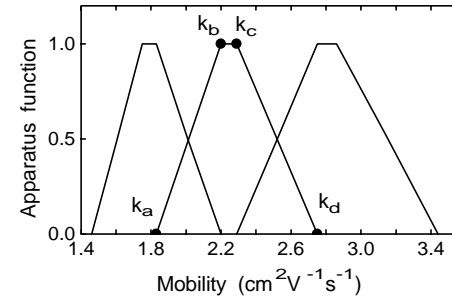


Figure 10. Apparatus functions.

As a result, a set of the charge density function $\rho(k)$ values at certain knot points of the spectrum (geometric mean of the mobilities of k_b and k_c in Figure 10) is given according to the piecewise linear approximation model [Tammet, 1980]. The fraction concentrations can be found by integrating over the mobility intervals.

A simplified method for the estimation of fraction concentrations (elementary charges per cm³ in a mobility range), without solving Eq. 6,

was applied in most sections of this paper (except Chapter 11). In that case, the spectrometer records are interpreted as fraction concentrations. The mobility boundaries of fractions are derived from the apparatus functions. The geometrical means of the limiting mobilities of k_a and k_b and of k_c and k_d are considered as conventional boundaries of fractions (Figure 10). The simplified method yields somewhat smoothed mobility spectra. However the differences, as compared to the stricter method, are small; uncertainties not exceeding a few per cent are expected for fraction concentrations [Tammet *et al.*, 1987a].

The recorded air ion mobility fractions and estimates of the equivalent diameter ranges of ion mobility assuming single-charged particles [Tammet, 1995] are presented in Table 2. Five classes of air ions established by means of statistical analysis are also given. The whole range of mobility is

logarithmically divided into 20 intervals: 9 intervals in the subrange of $0.00041\text{--}0.29\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and 11 intervals in the subrange of $0.25\text{--}3.2\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Thus each mobility spectrum consists of 20 fraction concentrations.

The spectrum of small ions is compiled of two successive measurements with voltages of 47.5 V and 150 V applied to the measuring condenser of IS₁. The concentration of negative ion fraction N₆ (for positive ions P₆) in Table 2 is an average of two overlapping fractions. The estimated systematic difference of the concentration in coinciding fractions is less than 2–3%. The corrections of the diffusion losses of air ions on the entrance channel parts of spectrometers have been made by relevant equations [Tammiet, 1970]. The correction factors are $1/(1 - 0.2 k^{0.67})$ and $1/(1 - 0.08 k^{0.67})$, where k is the mobility of ions, for spectrometer IS₁ and for IS₂+IS₃, respectively.

Table 2. Air ion fractions, estimates of equivalent diameter ranges assuming single-charged particles, and proposed classes of air ions. N_k and P_k are the symbols of fractions for negative and positive polarity, respectively.

Ana-lyzer	Fraction	Mobility $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$	Diameter nm
<i>Small Cluster Ions</i>			
IS ₁	N_1/P_1	2.51–3.14	0.36–0.45
IS ₁	N_2/P_2	2.01–2.51	0.45–0.56
IS ₁	N_3/P_3	1.60–2.01	0.56–0.70
IS ₁	N_4/P_4	1.28–1.60	0.70–0.85
<i>Big Cluster Ions</i>			
IS ₁	N_5/P_5	1.02–1.28	0.85–1.03
IS ₁	N_6/P_6	0.79–1.02	1.03–1.24
IS ₁	N_7/P_7	0.63–0.79	1.24–1.42
IS ₁	N_8/P_8	0.50–0.63	1.42–1.60
<i>Intermediate Ions</i>			
IS ₁	N_9/P_9	0.40–0.50	1.6–1.8
IS ₁	N_{10}/P_{10}	0.32–0.40	1.8–2.0
IS ₁	N_{11}/P_{11}	0.25–0.32	2.0–2.3
IS ₂	N_{12}/P_{12}	0.150–0.293	2.1–3.2
IS ₂	N_{13}/P_{13}	0.074–0.150	3.2–4.8
IS ₂	N_{14}/P_{14}	0.034–0.074	4.8–7.4
<i>Light Large Ions</i>			
IS ₂	N_{15}/P_{15}	0.016–0.034	7.4–11.0
IS ₃	N_{16}/P_{16}	0.0091–0.0205	9.7–14.8
IS ₃	N_{17}/P_{17}	0.0042–0.0091	15–22
<i>Heavy Large Ions</i>			
IS ₃	N_{18}/P_{18}	0.00192–0.00420	22–34
IS ₃	N_{19}/P_{19}	0.00087–0.00192	34–52
IS ₃	N_{20}/P_{20}	0.00041–0.00087	52–79

3.7. Measurement accuracy

The accuracy of the air ion mobility spectra measurements is determined by a composite uncertainty of estimating the mobility and the concentration of fractions.

The systematic instrumental uncertainty of the limiting mobilities of fractions is small, about 3–4%, because the main technical parameters of spectrometers (effective capacitance of measuring condenser, and applied voltage) are adjusted with the accuracy of more than 1%; the uncertainty of the flow rate was estimated 2%. The uncertainties of the fraction concentrations (at a confidence of 95%) are in the range of 4–7 cm^{-3} , 3–10 cm^{-3} and 10–60 cm^{-3} for spectrometers of IS₁, IS₂ and IS₃ considering the minimum and maximum values of measured concentrations, respectively.

The random components of the measurement uncertainties are determined by the uncertainties of the offset levels of spectrometers. The offset levels, determined mainly by the drift of the zero signals of electrometric amplifiers, are recorded continuously during the measurements, applying zero voltage to the DMA. The statistical uncertainties caused by random noise of the zero recordings are about 2–6 cm^{-3} , 2–10 cm^{-3} and 10–20 cm^{-3} for IS₁, IS₂ and IS₃, respectively, considering the 5-minute average spectra.

The extra measurements of the offset levels of spectrometers are carried out episodically, as a rule once or twice a month. The same measurement procedure as in the case of regular measurements is used, but without airflow through the spectrometers (ionization chamber measurements). This procedure enables to estimate also the measurement errors not taken into account by the first procedure (e.g. parasitic currents induced by switching and the instability of the high voltage, the polarization of insulators, and the radioactive contamination of the DMA). The mean offset levels corresponding to the mobility fractions of IS₁ are nearly zero with the statistical uncertainty of about 4–6 cm^{-3} , considering the 5-minute average spectra. The mean offset levels of IS₂ are commonly in the range of 2–6 cm^{-3} , and those of IS₃ in the range of 1–40 cm^{-3} , increasing with the decreasing of the limiting mobility of fraction. The uncertainties are about 3–8 cm^{-3} and 14–30 cm^{-3} for IS₂ and IS₃, respectively.

It follows that the first procedure completely accounts for the real offset levels of IS₁, but an extra procedure is necessary to determine the offset levels of IS₂ and IS₃ for more precise measurements of large ion concentrations.

The random component of the measurement uncertainty was also estimated during the relatively stable conditions (no trends in ion concentration), ignoring natural variability. The uncertainty of the fractions of IS₁ was 4–8 cm^{-3} , about 6–16 cm^{-3} for IS₂ and 20–60 cm^{-3} for IS₃. The lower the limiting mobility of IS₂ or IS₃, the higher was the uncertainty.

Considering the hourly average spectra used in the present work, the statistical uncertainties are about 3.5 times smaller.