Patience Clever was disappointed. She looked at the result of the round robin test and admitted that the value they had reported was far from the mean value and outside of the confidence range. They had failed the test although they had done their method development and analysis very carefully. She looked through the protocols once more and recapitulated: we standardized with an acidified $\text{Se}^{4+}$ solution in the range of 5–25 $\mu$g/L (0.15 ng–0.75 ng). Our calculated detection limit was about 1 $\mu$g/L in the solution for measurement and 3 $\mu$g/L based on undiluted serum. We stabilized Se with a Cu modifier which had already worked perfectly for many determinations in water samples. We even tried a mixture of Cu and Fe for comparison. The serum was diluted $1 + 2$, $15 \mu$L of the measurement solution were introduced into the tube and $10 \mu$L of the modifier were added. The sample was pyrolyzed carefully at $1000 ^\circ$C. Se was atomized at $2100 ^\circ$C, giving a good symmetric peak which returned to the baseline after 2 s. The diluted serum measurement gave an average reading of 20 $\mu$g/L (0.3 ng) with a precision of 3–5%. Standards with concentrations of 3.3, 6.6 and 16.6 $\mu$g/L were added to the serum and yielded a line with exactly the same slope as that for the aqueous calibration (the calibration graphs are displayed in Fig. 2.1). The extrapolated value was again 20 $\mu$g/L (0.3 ng). Nevertheless, the true concentration of Se in the serum was 90 $\mu$g/L rather than 60 $\mu$g/L. Patience sighed. What did we do wrong? After all this effort in calibration and checking an error is impossible! Why did the other labs get the right result? “One should invent a technique where you do the measurement on a sample and calculate the concentration in the sample just from physical constants; a kind of absolute analysis” and with a frown she grabbed the telephone to call the support desk of the instrument manufacturer.
2.1 Sensitivity and characteristic mass: the way to check your spectrometer

In spite of Patience Clever’s dream of absolute, standardless analysis, AAS is used as a relative analytical method. This means that the absorbance of an unknown sample is compared with the absorbances of so-called blank solutions – which represent the contamination level introduced by the laboratory environment and all reagents added to standards and samples – and with the absorbances of solutions containing known concentrations of the element(s) to be determined, the so-called reference solutions. The result of this instrument calibration is a blank absorbance value and a relation between analyte concentrations and absorbance values, the calibration curve. This relationship, the slope of the calibration curve or sensitivity, should be fairly constant [1] within narrow boundaries for a given experimental setup. It can therefore be used to check the correct function of the instrument on the one hand, and/or to recognize erroneous standard solutions or chemical conditions. In order to be able to quickly check on the sensitivity without the necessity to establish a calibration curve and in order to define sensitivity in absolute terms, the normalized reciprocal sensitivity, the so-called characteristic mass ($m_0$) was defined. $m_0$ is defined as the mass of analyte...