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A New, Accurate Single-Sinker Densitometer for Temperatures from 233 to 523 K at Pressures up to 30 MPa[1]

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A new apparatus for density measurements of fluids in the entire range from gas to liquid densities is presented. The instrument is a single-sinker buoyancy densitometer designed in a completely new way. The buoyancy force exerted by the sample fluid on an immersed sinker (buoy) is transferred by a new type of magnetic suspension coupling to an analytical balance. In order to reduce drastically the linearity error of the (commercial) balance, a special basic load compensation is applied which also avoids any buoyancy effect of the laboratory air on the balance. The new single-sinker densitometer covers a density range from 10 to 2000 kg · m^{-3} at temperatures from 233 to 523 K and pressures up to 30 MPa. A special compact version of such a single-sinker densitometer can even be used at temperatures from 80 to 523 K at pressures up to 100 MPa. Test measurements on densities of carbon dioxide at 233, 360, and 523 K at pressures up to 30 MPa show that the estimated total uncertainty of ±0.02% to ±0.03% in density is clearly met.

KEY WORDS: density; high pressure; high temperature; magnetic suspension balance; single-sinker densitometer.

1. INTRODUCTION

Based on our experience, nearly all of the currently used methods of densitometry have one or more of the following shortcomings:

- Limits with regard to the achievable accuracy.
- Need of calibration with reference fluids over the entire operational range.

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- Applicable only in a part of the entire density range of a fluid.
- Unsuitable for covering a wide range of temperature and pressure.
- Complexity of the method and the apparatus design.

The volumometers (piezometers and constant-volume cells) suffer above all from the fact that the determination of the cell volume as a function of temperature and pressure is difficult. For the Burnett method, the main difficulties are caused by adsorption of the gas on the inner surface of the measuring cell. The indirect methods, especially vibrating U-tube densitometers, vibrating-fork, and vibrating-cylinder densitometers, not only require calibration with reference fluids over the entire operational range, but also often require that calibration fluids have densities close to those of the fluids to be studied. Except for water and mercury, however, no liquid density is known accurately enough at elevated pressures and temperatures. The density values of water and mercury do not correspond, in most cases, to the density values required for the temperature and pressure range of the fluid to be studied.

In contrast to the indirect methods, hydrostatic weighing methods can be regarded as absolute density-measuring methods. When applying the Archimedes principle is its classical way, the density of a fluid is determined by measuring the buoyancy force exerted on an immersed sinker (buoy). Normally, the sinker is a simply shaped quartz-glass body (e.g., a sphere or cylinder) whose volume as a function of temperature and pressure can be very accurately ascertained. The calibration of the sinker at a single reference point (preferably at about 293 K and 0.1 MPa) can very easily be carried out and no further calibration is necessary. The major problem in applying this method at elevated pressures is the determination of the buoyancy force exerted on the sinker in the *pressurized* measuring cell. Many attempts have been made to measure the buoyancy force with a substitute for a balance which can be used *within* such a measuring cell; very recently, for example, a system was described where the sinker is suspended from a vibrating wire functioning as such a "balance" [1]. However, all such systems have the disadvantage that their sensitivity and accuracy are limited so that they only cover a part of the entire fluid region (usually the liquid range) with reasonable accuracy. About 10 years ago, however, a magnetic suspension coupling was developed to transfer the buoyancy force exerted on such a sinker through the wall of the pressurized measuring cell to a balance placed outside the cell at ambient conditions (laboratory atmosphere). This magnetic suspension coupling was one of the main features of the "two-sinker densitometer" with which very high accuracies in density measuring have been achieved (see Section 2).

It is the purpose of this paper to present a "single-sinker densitometer" in a completely new application whereby *all* the shortcomings listed previously are avoided and where operation even at high pressures is possible. Before describing this new single-sinker densitometer, the principle of the well-established two-sinker densitometer [2, 3] is briefly reviewed.

2. TWO-SINKER DENSITOMETER

At the beginning of the 1980s, Kleinrahm and Wagner [2, 3] developed a two-sinker buoyancy apparatus primarily designed and built for measuring the densities of the saturated liquid and vapor along the entire saturation curve of pure fluids. As a result of further development of this apparatus, it is also currently possible to perform density measurements over the entire density range from the dilute gas up to the compressed liquid, and also in the critical region. This apparatus covers a temperature range from 80 K (in the near future from 60 K) to 360 K, a pressure range from 0.0001 to 12 MPa, and a density range from 1 to 2000 $kg \cdot m^{-3}$. Due to the use of *two specially matched sinkers*, all the effects (such as zero-point shift of the balance, buoyancy forces on auxiliary devices, surface tension, adsorption effects) which reduce the accuracy of density measurements by applying the "normal" Archimedes principle with only one sinker are *automatically compensating*. Based on this compensation principle, a very small uncertainty in density measurement of less than $\pm 0.015\%$ is achieved in nearly the entire measuring range. Since putting this equipment into operation, the density behavior of the technically and scientifically most important substances has been systematically investigated. Up to now, methane [2–6], carbon dioxide [7–9], and argon [10, 11] have been measured in the entire fluid region covered by this apparatus; N_2, SF_6, R12, R22, and natural gas have been measured in parts of the fluid region.

It can be concluded that, in its present version, this two-sinker densitometer avoids the shortcomings listed in Section 1, except for the last two items.

3. THE NEW SINGLE-SINKER DENSITOMETER

Due to the necessity of two sinkers with their sophisticated sinker-changing device, the two-sinker densitometer is rather complex and the special advantage of this method (high accuracy even at *very low* gas densities) is of minor importance for most applications. Therefore, in order to simplify the density measurements at medium and high densities without any substantial loss of accuracy in comparison with the two-sinker densitometer and to enlarge the operational range toward higher pressures and

temperatures, we have developed a new type of single-sinker densitometer. By applying some of the advantageous features of the two-sinker principle, also with the new single-sinker densitometer very low uncertainties of mostly less than $\pm 0.02\%$ in the density measurement can be achieved, except at very low gas densities.

Since a basic element of the new single-sinker densitometer is a new type of magnetic suspension balance which is an advancement of the former version [12] used for the two-sinker densitometer, this new magnetic suspension balance is described first.

3.1. New Magnetic Suspension Balance

The new magnetic suspension balance for various applications (e.g., density measurements, sorption measurements, solubility of gases in liquids and solids, investigation of corrosions and other chemical reactions) is described in detail by Lösch et al. [13, 14]. Here, only the main features with regard to density measurements are summarized.

Figure 1 shows the basic design of the magnetic suspension balance and the controlling principle of the magnetic suspension coupling, which is the main part of this instrument. The magnetic suspension coupling consists of an electromagnet and a permanent magnet. The electromagnet is attached at the underfloor weighing hook of a commercial analytical balance or microbalance. Inside the coupling housing, there is a permanent magnet to which the sample (load) to be investigated is linked by means of a load coupling and decoupling device (for density measurements, the sample is replaced by a sinker; see next subsection). The upper part of the coupling housing, which separates the permanent magnet from the electromagnet, is manufactured of a magnetically neutral metal, namely of copper beryllium or copper chrome zircone.

To achieve the freely suspended state of the permanent magnet, its absolute position is detected by a position sensor and controlled in a direct and fast loop (PID controller). By means of a superimposed set-point controller and an additional control system, several vertical motions of the permanent magnet are generated automatically. In this way, soft up- and downward movements of the permanent magnet can be realized and via the load coupling and decoupling device the measuring load can be coupled and decoupled. This measuring load decoupling, carried out automatically by the suspension coupling itself, is one of the great advantages of the new controlling principle. Its application to density measurements is explained in the next subsection. The magnetic suspension coupling does not influence the accuracy of the balance (resolution ± 0.000001 g).

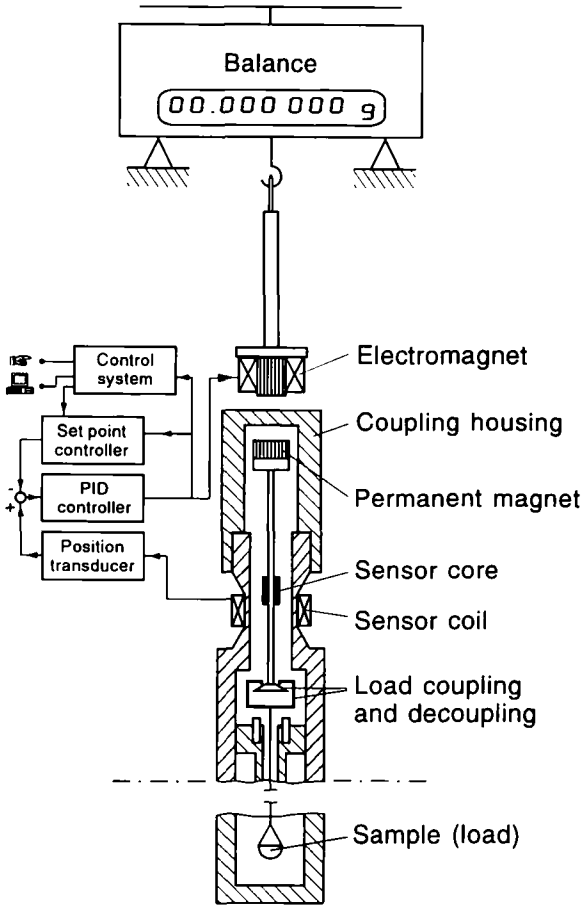

Fig. 1. Principle of the new magnetic suspension balance.

It should be pointed out that in the meantime such magnetic suspension balances (this means all parts above the dashed-dotted line in Fig. 1) are commercially available,[5] so that a single-sinker densitometer can be designed relatively simply using such instruments.

3.2. Principle of the New Single-Sinker Densitometer

The single-sinker densitometer is based on a buoyancy method, where, however, the Archimedes principle is applied in a new way. The main part

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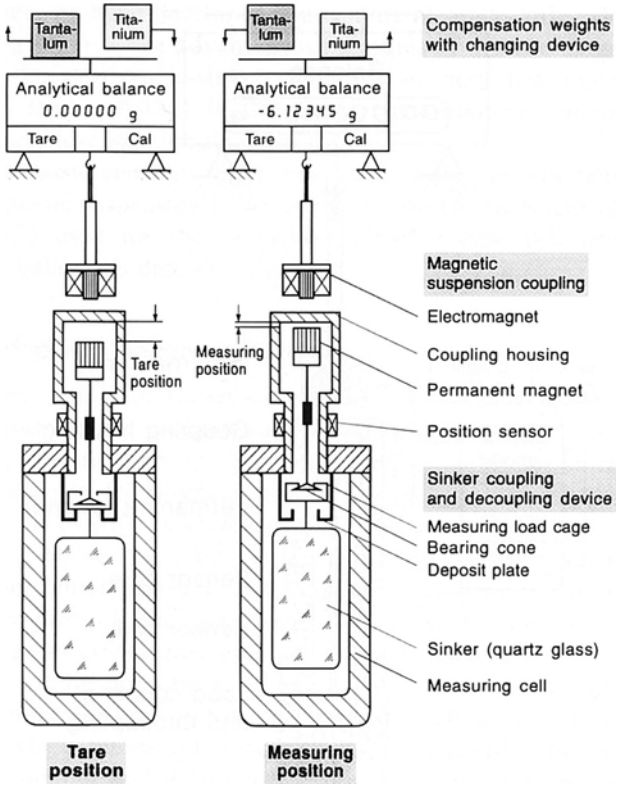

Fig. 2. Principle of the new single-sinker densitometer with basic load compensation.

of the new instrument is the magnetic suspension balance described in the preceding subsection. Instead of the sample, a solid quartz-glass cylinder working as a sinker (volume $V_S \approx 26\ cm^3$) is suspended from the load coupling and decoupling device.

Figure 2 illustrates the principle of the "new single-sinker method." The controlling system of the magnetic suspension balance (see Fig. 1) is not shown. In the tare position, the permanent magnet of the magnetic suspension coupling is suspended at a relatively large distance from the top of the coupling housing. In this position, the sinker is decoupled from the permanent magnet via the coupling and decoupling device (no connection between the bearing cone and the measuring load cage, which rests on the deposit plate); the balance can be tared to zero. In order to achieve the measuring position, the electronic controlling unit of the magnetic

suspension coupling brings the permanent magnet closer to the top of the coupling housing. This means that also the bearing cone moves upward and takes the measuring load cage with which the sinker is connected. In this way, the sinker is coupled with the balance (via the magnetic suspension coupling). In this position, the sinker is weighed.

In order to achieve high accuracy even at relatively low densities, the balance is only operated near its zero point by a basic load compensation as follows (see Fig. 2): In the tare position a tantalum ($\rho = 16.7\ \mathrm{g \cdot cm^{-3}}$) weight (about 80 g) is on the balance. During the switch to the measuring position, the tantalum weight is automatically exchanged with a titanium ($\rho = 4.5\ \mathrm{g \cdot cm^{-3}}$) weight of about 20 g. Since in this position the sinker (the mass of the sinker is $m_S \approx 60$ g) is coupled with the balance, the total load of the balance is again about 80 g (as in the tare position). In this way, the linearity error of the balance is drastically reduced. Since the two weights have the same volume, the buoyancy effect of air on the weights is compensated as well.

In order to measure the density of the fluid in the measuring cell, the sinker is coupled and decoupled several times (changes between the tare and measuring positions) to improve the accuracy of the mass measurement by averaging. Then, the density of the fluid is determined from the simple relation

$$\rho = \frac{m_S - m_S^*}{V_S(T, p)} \tag{1}$$

In this equation, m_S is the "true" mass of the sinker (weighed in the evacuated measuring cell), m_S^* is the "apparent" mass of the sinker (weighed in the fluid-filled measuring cell), and $V_S(T, p)$ is the temperature- and pressure-dependent volume of the sinker. The value of $V_S(T, p)$ is known from calibration with water at 20°C and 0.1 MPa (calibration uncertainty $\leqslant \pm 0.003\%$). The dependence of the volume of quartz-glass on temperature and pressure is known accurately [15].

This new single-sinker method compensates all side effects which drastically reduce the accuracy when the Archimedes principle is used for density measurements in its classical application. The gas adsorption on the sinker is the only effect which, in contrast to the two-sinker method, is not compensated. This adsorption, however, effects the accuracy only at very low gas densities and is clearly smaller in comparison with the other absolute density-measuring methods (Burnett, constant-volume cells, etc.) In our method, both surface area and surface roughness of the sinker are much smaller than in the other devices (and the sinker does not have any sealing splits, thread splits, and soldering joints).

Based on this new application of a single-sinker buoyancy method, an uncertainty in the density measurement of less than $\pm(0.01\,\% + 0.002\,\mathrm{kg \cdot m^{-3}})$ can be achieved; for the current achieved uncertainty see next subsection.

3.3. Description of the Apparatus

Figure 3 shows the basic design of the new high-temperature, high-pressure densitometer. It consists of the measuring cell with the sinker (the volume filled with the fluid to be measured corresponds to the shaded area), the magnetic suspension coupling (Rubotherm, Germany), the analytical balance (Mettler AT201, Switzerland), an inner and outer double-wall thermostat, and a vacuum vessel for the insulation of the two-stage thermostat. Depending on the temperature range, ethanol

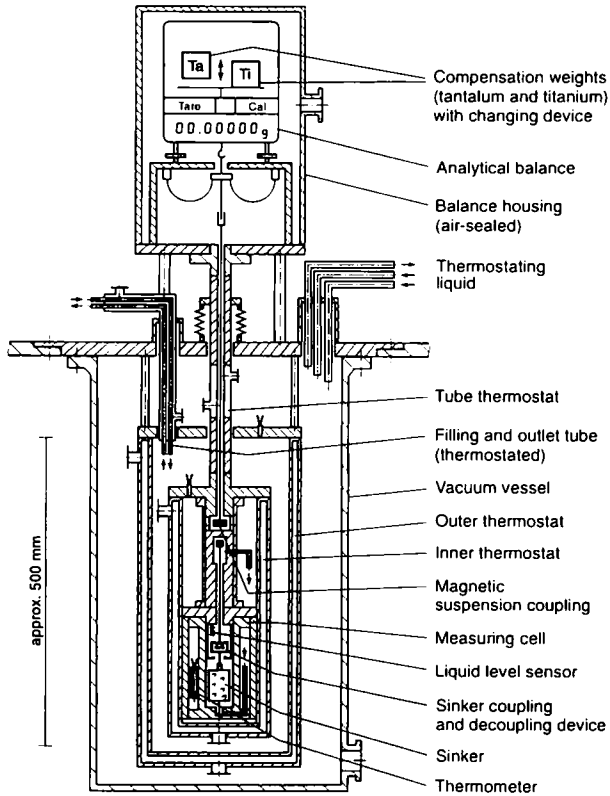

Fig. 3. Basic design of the high-temperature, high pressure densitometer.

(233–313 K), water (283–363 K), and polyalkylene glycol (353–523 K) are used as thermostatting liquids; they are prethermostatted outside the vacuum vessel by a special thermostat (Huber Unistat 380W HT, Germany). The temperature is measured by a 25-Ω platinum resistance thermometer (Rosemount 162D, USA) in connection with a resistance measuring bridge (Automatic Systems Laboratory F700A, UK). The uncertainty in the temperature when local temperature gradients and temperature stability are taken into account is less than ± 0.005 K. The pressure is measured with a piston manometer and a piston barometer (Desgranges et Huot 5200S[2] and 2171, France) via a differential pressure indicator (Rosemount 1151, USA); the uncertainty in the pressure measurement is less than $\pm 0.006\%$ except for very low pressures. The measuring cell can be filled through two tubes which also allow the entire system to be flushed. For measuring the densities of *saturated* liquids, a liquid-level-indicator is placed in the upper part of the measuring cell (see Fig. 3). Further details of the design of this apparatus and of its handling are given by Brachthäuser et al. [15].

At present, the new densitometer covers a density range from 10 to 2000 kg · m^{-3} at temperatures from 233 to 523 K and pressures up to 30 MPa. The uncertainty in the density measurement which has been achieved up to now is less than $\pm(0.015\% + 0.003\ \text{kg} \cdot \text{m}^{-3})$. Together with the uncertainty in the temperature and pressure measurement, a *total* uncertainty in density of less than $\pm(0.02\text{–}0.03)\%$ has been achieved with the exception of low gas densities (below about 50 kg · m^{-3}). This uncertainty value will very likely be reduced in the future.

The operational range with regard to temperature and pressure given above only relates to this apparatus and not to the new single-sinker method in general. In Section 4, a very compact version of such a single-sinker densitometer is briefly presented which is able to cover a much wider range of temperature and pressure.

3.4. Test Measurements on Carbon Dioxide

In order to check the new apparatus, density measurements on carbon dioxide have been carried out on three selected isotherms. The first isotherm, $T = 233.15$ K, corresponds to the lowest operational temperature of the apparatus and covers mainly the liquid phase of CO_2. The second isotherm, $T = 360$ K, lies in the middle of the temperature range covered by the apparatus and is about 56 K above the critical temperature; and the third isotherm, $T = 523.3$ K, corresponds to the upper temperature limit of the apparatus.

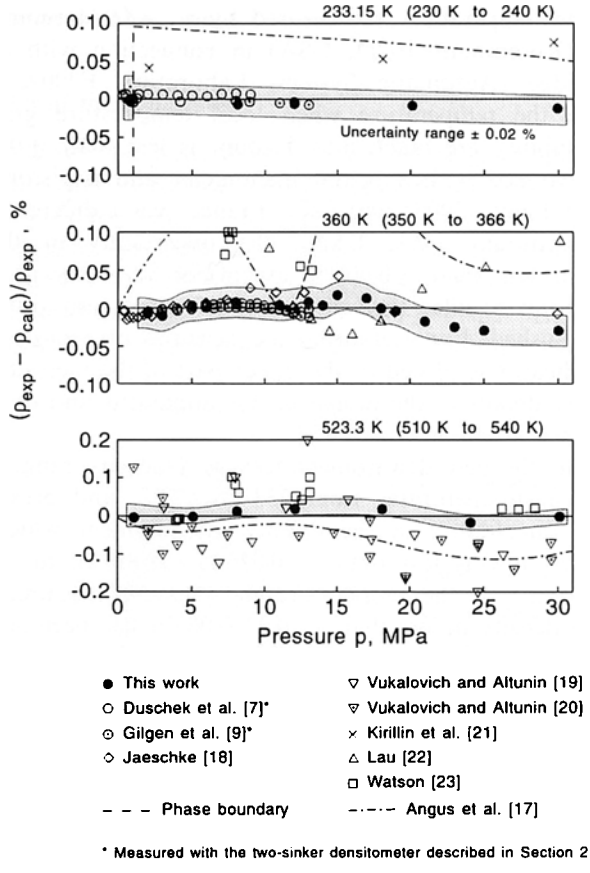

Fig. 4. Test measurements of densities of carbon dioxide taken with the new apparatus in comparison with experimental densities of other authors and with those values (zero line) calculated from a new equation of state [16]; values calculated from the IUPAC equation of state [17] are plotted for comparison. The dotted area corresponds to the experimental uncertainty of the test measurements in this work. The temperature range given in brackets above the deviation diagrams corresponds to the temperature range covered by the experimental densities taken from literature.

Figure 4 shows a comparison of these test measurements, taken with relatively large steps in pressure, with data sets of experimental densities from the literature, and with values calculated from a new equation of state for CO_2 recently developed by Span and Wagner [16]. It can be seen that the test measurements are in excellent agreement, namely clearly within $\pm 0.01\%$, with the densities measured by Duschek et al. [7] and by Gilgen et al. [9] at 240 and 360 K; these data were measured with the two-sinker densitometer mentioned in Section 2. Moreover, the agreement with Jaeschke's data [18] at 353 K is also very good. The deviation of the test measurements from values calculated from the equation of state by Span and Wagner [16] remains everywhere clearly within the uncertainty of the equation, which amounts to $\pm 0.03\%$ in density for $p \leqslant 13$ MPa and $T \leqslant 360$ K, $\pm 0.05\%$ in the adjacent range up to 30 MPa and 480 K, and $\pm 0.1\%$ for higher temperatures. These comparisons show that the estimated low experimental uncertainty given in Section 3.3 is clearly met.

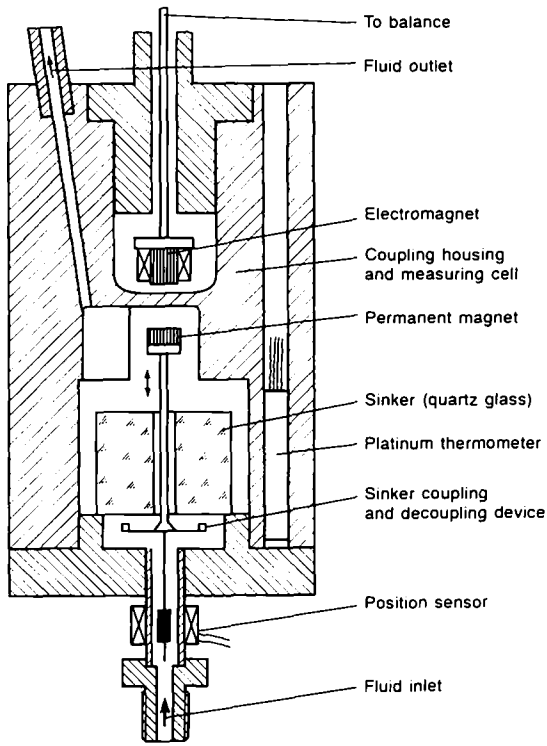

Fig. 5. Principle of a compact single-sinker densitometer.

4. COMPACT SINGLE-SINKER DENSITOMETER

In order to simplify further such a single-sinker densitometer we have designed a very compact version; Fig. 5 shows the basic design of the inner part of such an instrument. Here, the coupling housing of the magnetic suspension coupling and the measuring cell have been unified, which yields a very compact body with a very small measuring cell requiring only a small amount of sample fluid. Due to this compact design the operational range with regard to pressure extends up to very high pressures, namely up to 100 MPa. Moreover, by cooling with liquid nitrogen and corresponding electrical heating (not shown in Fig. 5), a temperature range from 80 to 523 K can be covered. To achieve even higher operational temperatures we are working on a modification of the magnetic suspension coupling which can be used up to 673 K.

5. CONCLUSION

A single-sinker densitometer has been designed and built which employs a new type of buoyancy densitometer with one sinker. The basically new feature of the instrument is a new type of magnetic suspension balance in connection with a special basic-load compensation. The new method has drastically increased the accuracy of the density measurements in comparison with a single-sinker densitometer in its classical design. The operational range of the instrument covers the entire density range from gas densities to liquid densities at temperatures from 233 K (limited by the present thermostat; temperatures down to 80 K are generally possible) to 523 K and pressures up to 30 MPa. Test measurements on carbon dioxide at 233, 360, and 523 K at pressures from 0.8 to 30 MPa have confirmed the estimated total uncertainty in density of less than $\pm 0.02\%$ to $\pm 0.03\%$; the reliability of these uncertainties was estimated to be about 95%.

The briefly described new compact single-sinker densitometer can even be used for pressures up to 100 MPa.

Based on our present knowledge, we believe that this new single-sinker method will develop into a widely used procedure in densitometry because of its potential high accuracy in combination with rather a simple design and a large operational range with regard to temperature and pressure.

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the basic load compensation and for his assistance in developing the new compact single-sinker densitometer. Above all, we thank the Deutsche Forschungsgemeinschaft for financial support of our work.

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