*International Journal of Thermophysics, Vol. 16, No. 2, 1995*

# Dynamic Viscosity Measurements by Photon Correlation Spectroscopy[1]

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It is shown that absolute values for the dynamic viscosity of liquids can be obtained using photon correlation spectroscopy. The technique is based on the measurement of the particle diffusion coefficient of spheres dispersed in a liquid. In the experiments both PMMA and silica particles were used as a seed. This includes the first application of newly industrially produced silica samples for the goal of viscosity measurements. Experiment results are presented for various liquids at ambient conditions, including some alcohols, alkanes, and the refrigerant R123. Most of the data agree quite well with reference values. Requirements for suitable seed particles and possible reasons for deviations from reference data are discussed. Measurements in liquid mixtures indicate the general possibility for the simultaneous determination of dynamic viscosity and molecular diffusion coefficient in a single experiment.

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**KEY WORDS:** particle diffusion; photon correlation spectroscopy; R123; viscosity.

## 1. INTRODUCTION

Today there exist a variety of widely accepted measurement techniques for the determination of the dynamic viscosity of liquids; see, e.g., Ref. 1. Various comparison studies show, however, that the differences in the results published for some liquids, especially new environmentally acceptable refrigerants, exceed the mutual uncertainty quoted by the individual investigators [2–4]. Although this effect is in part ascribed to possible impurities of the samples, it is nonetheless desirable to have an additional,

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[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

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independent method for measuring this quantity. Thus, the main aim of this paper is to investigate if photon correlation spectroscopy (PCS), often also called dynamic light scattering, can be a useful supplementary technique.

PCS has proven to be a successful tool both for the determination of particle sizes and the measurement of various thermophysical properties of transparent fluids, including the transport properties thermal diffusivity and binary diffusion coefficient [5–8]. Trying to extend this method to viscosity measurements is a challenging and interesting aim because by this method various required thermophysical properties, espcially for new working fluids, could be easily and consistently obtained. Besides other fundamental advantages, an interesting feature of PCS is that, in contrast to other techniques for measuring viscosity, there is no energy input into the sample apart from the low-power probing laser beam. There have been some successful attempts to use this method for the determination of the dynamic viscosity of liquids [7, 9], with specialized experimental arrangements even up to pressures of 2.9 GPa [10]. The liquids investigated include water and various alcohols, hydrocarbons, and mixtures of these. These investigations, however, suffer from the fact that manufacturers' values for the particle size were used or the required calibration of particle sizes was done by using tabulated viscosity values of the liquid under investigation. These limitations thus allow only the determination of relative changes of viscosity due to changes of temperature and pressure. In this paper results are presented where particle diameters are obtained from calibration measurements in liquids of given viscosities; then these values are used for determining the absolute viscosity of other liquids.

## 2. PRINCIPLES OF THE TECHNIQUE

### 2.1. Method

The basis of dynamic light scattering for dynamic viscosity measurements is the dispersing of particles of known size into the liquid of interest and measuring the mean square displacement of the particles (see, e.g., Ref. 5). For freely diffusing particles the particle diffusion coefficient $D_p$ is related to particle diameter $d$ and dynamic viscosity $\eta$ via the Stokes–Einstein relationship:

$$D_p = \frac{kT}{3\pi\eta d} \qquad (1)$$

where $k$ is Boltzmann's constant and $T$ is the temperature of the sample.

The diffusion coefficient is obtained by evaluating the time-dependent homodyne autocorrelation function

$$g^{(2)}(t) = a + b\exp(-t/\tau_c) \tag{2}$$

with experimental constants $a$ and $b$ for the decay time $\tau_c$ and with

$$D_p = 1/(2q^2\tau_c) \tag{3}$$

Here $q$ is the modulus of the scattering vector of the optical arrangement, given by

$$q = \frac{4\pi n}{\lambda_0}\sin\frac{\Theta}{2} \tag{4}$$

where $n$ denotes the refractive index of the liquid investigated, $\lambda_0$ is the laser wavelength *in vacuo*, and $\Theta$ is the scattering angle.

## 2.2. Requirements for Seed Particles

A basic requirement for seed particles applicable to viscosity measurements is their mean diameter, which should be within a range of some 20–500 nm. These limits are not fundamental, and there have indeed been dynamic light scattering experiments reported with particles outside of this range, yet they pose practical guidelines for the experimenter.

One major reason for avoiding very small particles is their low scattering power, which scales with $d$ to the sixth power in this range, thus resulting in weak signals, especially when one works with low-power laser sources and at the low particle concentrations required. In using very large particles, problems with particle sedimentation increase as Brownian agitation is no longer able to keep the particles in a stable dispersion. Moreover, the scattering form factors show pronounced minima, while rapidly ocillating with the scattering angle. This point implies serious problems, especially when another basic requirement, namely choosing particles with a very small degree of polydispersity, is not fulfilled. The mean diffusion coefficient in a light scattering experiment, which as a matter of principle originally is always an intensity-weighted quantity, heavily depends on the scattering vector employed. This property has in turn been used to determine small polydispersities in particle size [11]. On the other hand, trying to perform light scattering experiments with very small particles, it is very difficult to find particles with a small degree of polydispersity, as many particles of practical use are produced in a growth process, where uniformity, to a certain extent, is improved with increasing particle size. The requirement of particle monodispersity also implies the absence of agglomerates in the dispersion. In order to achieve this goal two basic mechanisms of particle stabilization are known, steric and electrostatic stabilization, which are treated in great detail in the numerous textbooks on colloidal chemistry or by papers of the groups active in this field [12–14].

Another difficulty is the possible swelling of particles in certain solvents. Here care must be taken above all when using polymeric particles such as polystyrene or PMMA. Penetration of solvent molecules into the particles may result in a dramatically increased diameter [15].

## 3. EXPERIMENTS

### 3.1. Particles Used and Sample Preparation

In this work mainly silica particles were used as a seed. These exhibit excellent chemical stability and can be obtained readily modified with various surface treatments. Laboratory samples were dry particles coated with stearylalcohol, with a nominal diameter of 242 nm and a polydispersity of 7%, and spheres coated with 3-methacryloxypropyltrimethoxysilane (TPM), dispersed in ethanol, with a nominal sphere diameter of 180 nm and a polydispersity of 8%. PCS for viscosity measurements would strongly benefit from a possible use of industrially produced particles. Today there are such silica spheres without and with various surface treatments available, which, to our knowledge, have not been employed for viscosity measurements before. In first experiments we used commercial silica in the form of dry native particles with a nominal diameter of 250 nm, supplied without an additional surface treatment.

In addition a sample of PMMA particles, dispersed in decalin, was investigated. These had a nominal diameter of 420 nm with a standard deviation of 4% and were supplied surface-modified by poly-(12-hydroxystearic acid) (PHSA).

Dried particles and master suspensions were directly dispersed into the liquids under investigation and submitted to ultrasonic treatment for up to several hours. In the case of particles already dispersed in a liquid (ethanol or decalin) different particle concentrations implied various contaminations of the liquids under investigation by the original solvents with a maximum volume fraction below $2 \times 10^{-3}$. The remainder of the original solvent is thus negligible in most cases.

The solvents employed were in general of analytical grade with specified purities exceeding 99.5% by weight. Dry acetone was used (water content below 0.02%), as were some samples of the other solvents. Higher alkanes and alcohols were of synthetic grade with specified purities better than 99%. R123 (nominal purity 99.9%) and the oil labeled 3527 (ISO 15) were used as supplied. Water was purified by a milli-Q system.

Sonicated dispersions of silica samples were directly filtered into clean cuvettes by means of syringe filters with 0.45 $\mu$m pore size. For the PMMA particles, filters with a pore size of 1.2 $\mu$m withheld too many of the particles, so the dispersions were used without filtration. No signs of dust or initial agglomerates were visible in the measurements. For all combinaions of seed particles and solvent at least two, and normally three or four different particle concentrations were used in the measurements. Because of the unknown filter efficiency it is difficult to judge exactly the concentration of the silica samples investigated, but from comparisons of scattered intensity with unfiltered samples an upper limit for the particle volume fraction of $2 \times 10^{-4}$ may be assumed, as was also the case with the PMMA particles.

### 3.2. Experimental Setup and Procedure

The setup for the measurements is described in more detail elsewhere [16]. Light from a vertically polarized, 10-mW He–Ne laser is focused into a square cuvette. In some measurements, especially for extremely dilute samples, an Ar-ion laser was employed, typically operated at 50 mW. Signals from the photomultiplier tube were amplified, discriminated, and fed to a multiple-tau single-board correlator. The experiments were performed at ambient temperature near 20°C. Temperature was measured via a calibrated 100-$\Omega$ platinum resistance thermometer and was stable to better than 0.1°C during one experimental run. For data evaluation the mean value of the temperature at the beginning and at the end of the run was taken.

In order to achieve reliable results it is of extreme importance to ensure the agreement of the autocorrelation function with its theoretical form as given in Eq. (2) and thus to exclude possible distortions like multiple scattering, heterodyne mixing, particle agglomeration, or particle interactions. For this aim the experimental data were analysed by a multifit evaluation as described in Ref. 16. Additionally, a cumulant expansion [17] was performed, using an upper acceptance limit of 0.02 for the quality factor $Q = K_2/K_1^2$.

For detecting systematic deviations it is also helpful to use various particle concentrations and various scattering vectors. For the results reported here, normally three different particle concentrations and at least three different scattering vectors were realized for all combinations of particles and liquids.

## 4. RESULTS AND DISCUSSION

The results obtained with the various particles are summarized in Tables I–IV. The PCS results are modified for a 293.15 K (20°C) value via a modified Arrhenius equation of the form $\ln \eta = a + b/T + c/T^2$ $(+d/T^3)$, established by means of reference values. In the tables, the mean values are given together with their standard deviation. The reference values were in part obtained by performing our own regressions (denoted as Reg) from a series of literature data with the help of the MIDAS database of the University of Stuttgart [18]. We excluded values deviating more than 3% from the mean. In the instances of our own regressions the $\delta(\sigma)_{\mathrm{ref}}$ values are the standard deviations of the accepted data, while for reference values from the literature the claimed accuracy is given. For the paraffin oil only a typical value quoted by the distributor was available.

To use PSC as a method for determining absolute viscosity values, a calibration of particle size is essential. This is preferably performed in liquids showing similar properties to those to be investigated. For stearyl-coated silica this calibration was done in cyclohexane, an often-employed model solvent for these particles. An average diameter of 235.8 nm (viscosity of cyclohexane used: 0.975 mPa · s at 20°C) with a standard deviation of the measurements of 1.3% was obtained. The size of TPM-coated silica particles was determined as 172.2 nm ± 1.2% in water ($\eta_{20\,^\circ\mathrm{C}} = 1.002$ mPa · s) and 171.7 nm ± 1.0% in ethanol; we used the mean value of 172.0 nm for further evaluation. The diameter of the uncoated silica spheres was 215.0 nm ± 0.7%, as measured in water; that of the PMMA spheres was 427.9 nm ± 2.4%, as determined in *n*-dodecane ($\eta_{20\,^\circ\mathrm{C}} = 1.487$ mPa · s).

The hard-sphere behavior of stearyl-coated silica (Table I) in many instances is notable, yet it is known that flocculation may occur, depending on the quality of the solvent. In contrast to other authors [19], we have not been able to obtain stable silica dispersions in dodecane, probably due

**Table I.** Experimental Viscosities: Stearyl-Coated Silica Suspensions

| Liquid | $\eta_{20\,^\circ\mathrm{C}}$ (mPa · s) | $\sigma$ (%) | $\eta_{\mathrm{ref}}$ (mPa · s) | $\delta(\sigma)_{\mathrm{ref}}$ (%) | Ref.[a] |
|---|---|---|---|---|---|
| *n*-Pentane | 0.228 | 1.8 | 0.228 | 1.5 | Reg |
| Acetone | 0.337 | 0.9 | 0.318 | 3 | 21 |
| *n*-Heptane | 0.401 | 1.1 | 0.410 | 0.5 | 4 |
| Toluene | 0.581 | 1.6 | 0.589 | 0.6 | Reg |
| Paraffin oil (Iso 15) | 38.9 | 1.8 | 40.9 | — | — |

[a] See text for the significance of "Reg."

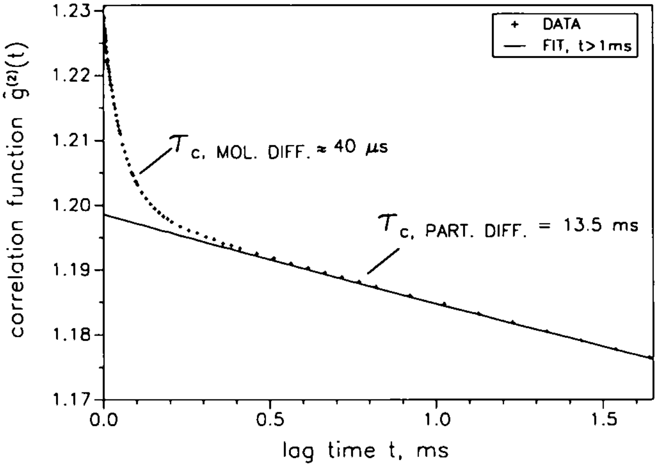

**Fig. 1.** Separation of light scattering signals originating from particle and molecular diffusion coefficients in paraffin oil.

to the larger diameter in our case: even at low concentrations we observed the formation of aggregates, with the effective diameter doubling in a few hours. This was one of the reasons for trying the PMMA particles for the higher alkanes in later experiments.

Particularly interesting observations were possible in the experiments with the paraffin oil. A SFC analysis of the oil revealed various hydrocarbons with chain lengths roughly between C16 and C36. By a fit of the autocorrelation function with omission of the channels up to a lag time of about 1 ms, a single-exponential component with a decay time of 13.5 ms was found to represent the particle diffusion coefficient. The initial part of this component can be identified in the right-hand side of Fig. 1. The figure also shows an additional signal in the first part of the autocorrelation function with a decay time of roughly 40 $\mu$s. This contribution represents a mixture of molecular diffusion coefficients due to the individual constituents of the oil. A similar signal can be observed when performing a light scattering experiment without tracer particles. The consequences of these observations are twofold. On the one hand, molecular diffusion in liquid mixtures does not form an obstacle for measuring viscosities, because of the difference in decay times. On the other hand, a prospect opens of determining viscosity and molecular diffusion in a single experiment.

TPM-coated silica (Table II) is well suited as a seed in polar liquids, where stabilization is achieved by a combination of steric and charge effects [20]. Experimental results for the refrigerant R123 in a somewhat extended

**Table II.** Experimental Viscosities; TPM-Coated Silica Suspensions

| Liquid | $\eta_{20°C}$ (mPa · s) | $\sigma$ (%) | $\eta_{ref}$ (mPa · s) | $\delta(\sigma)_{ref}$ (%) | Ref.[a] |
|---|---|---|---|---|---|
| Acetone | 0.337 | 1.3 | 0.318 | 3 | 21 |
| R123 | 0.433 | 1.2 | 0.441 | 3 | 3 |
| Methanol | 0.577 | 1.8 | 0.587 | 0.9 | Reg |
| 2-Propanol | 2.45 | 1.0 | 2.40 | 1.6 | Reg |
| 1-Hexanol | 5.28 | 0.8 | 5.24 | 1.9 | Reg |
| 1-Octanol | 8.84 | 1.1 | 8.81 | 1.3 | Reg |
| 1-Undecanol | 16.8 | 1.5 | 17.2 | 2 | 25 |

[a] See text for the significance of "Reg."

temperature range are published elsewhere [8]. The experiments with commercial, uncoated silica spheres (Table III), which inherently exhibit an electrostatic stabilization in polar solvents, showed absolutely satisfying correlation functions with a small standard deviation of the results.

Suitably coated PMMA particles (Table IV) offer good dispersion properties in various solvents. Three particular experimental observations are worth mentioning. The particles were completely dissolved in toluene within minutes, so viscosity measurements were not possible in this solvent. In acetone a value for the particle diameter was measured that was increased by ~75%. This is attributed to particle swelling. Finally, the measurements in pentadecane revealed signs of particle agglomeration in samples set at rest for more than 1 day. Using feshly prepared dispersions, we found that the particle performed as well as in other alkanes. It can be clearly seen from Table IV that the standard deviations of the measurements are in general larger than those of the experiments with silica particles. Here strong variations of the viscosity, or of the apparent particle diameter, could be observed with different scattering vectors. From these results the conclusion may be drawn that the employment of comparatively large particles for viscosity measurements is cumbersome, even if they only exhibit moderate polydispersity. Besides trying to achieve the use of highly monodisperse particles, smaller spheres are then favorable in order to

**Table III.** Experimental Viscosities; Commercial Native Silica Suspensions

| Liquid | $\eta_{20°C}$ (mPa · s) | $\sigma$ (%) | $\eta_{ref}$ (mPa · s) | $\delta(\sigma)_{ref}$ (%) | Ref.[a] |
|---|---|---|---|---|---|
| Acetone | 0.339 | 1.2 | 0.318 | 3 | 21 |
| Ethanol | 1.18 | 0.7 | 1.20 | 0.64 | Reg |
| 1-Undecanol | 17.0 | 0.8 | 17.2 | 2 | 25 |

[a] See text for the significance of "Reg."

Table IV. Experimental Viscosities; PHSA-Coated PMMA Suspensions

| Liquid | $\eta_{20°C}$ (mPa · s) | $\sigma$ (%) | $\eta_{\mathrm{ref}}$ (mPa · s) | $\delta(\sigma)_{\mathrm{ref}}$ (%) | Ref.[a] |
|---|---|---|---|---|---|
| *n*-Octane | 0.556 | 2.7 | 0.541 | 0.5 | 4 |
| *n*-Decane | 0.902 | 2.8 | 0.916 | 0.5 | 4 |
| 2-Propanol | 2.52 | 1.2 | 2.40 | 1.6 | Reg |
| *n*-Pentadecane | 2.98 | 3.2 | 2.89 | 1.4 | Reg |

[a] See text for the significance of "Reg."

avoid pronounced oscillations of the scattered intensity in the range of scattering vectors normally employed for PCS.

Most of the data presented here agree well with the literature viscosity values, given problems of sample purity, especially for higher alcohols and alkanes and also in a few instances with residuals of the original solvents, and of uncertainties due to particle polydispersity, especially with large particles. What is striking, however, are the marked deviations for the acetone values from Ref. 21, which occur for all three kinds of silica particles used here, showing a remarkable consistency of the PCS data. It is difficult to give a satisfying explanation. The values of the regression in Ref. 21 agree reasonably well with data given by individual experimenters, e.g., Bauer and Meerlender [22]. These authors point out that a possible water content of acetone may cause a distinct increase of the viscosity value. For this reason we used acetone with a water content below 0.02 wt% and carefully avoided contact with air humidity by using argon as an inert gas during sample preparation. Neither did an NMR analysis of the acetone samples used with both kinds of coated silica reveal significant traces of water or other impurities or side reactions. A possible electrostatic effect between solvated particles should depend on the particle volume fraction; the experiments have not shown such a dependence. Neither have there been signs of agglomeration. A tentative explanation is finally based on an effect connected with the charged particles and the acetone molecules. It is well known (see, e.g., refs. 23 and 24 and references therein) that the diffusion coefficient as given by Eq. (1) may be altered for charged colloidal particles by a friction factor $\zeta^{\mathrm{el}}$ due to the electrostatic interaction of the charged particle surface with the surrounding layer of solvent constituents, which adds to the Stokes term $\zeta^{0} = 3\pi\eta d$. This friction term would result in a smaller diffusion coefficient and thus in a larger apparent size or viscosity. It is not clear, however, why this effect should show up only with acetone and not with water and the alcohols probed with electrostatically stabilized silica. Such an additional friction factor may be responsible (besides possible swelling) for the increased viscosity value of 2-propanol in the case of the PMMA particles, and erroneous results may occur whenever particles sterically stabilized for apolar solvents are used in polar liquids. In order to elucidate the question of the deviating acetone results it may be helpful to perform further measurements both with more solvents, such as other ketones, and with particles of significantly different diameters, as the influence of an electrostatic friction factor should scale with particle size.

## 5. CONCLUSION

The results presented indicate that photon correlation spectroscopy can be used for absolute measurements of the dynamic viscosity of liquids. The advantage of this technique is that the liquid is studied in equilibrium. The availability of commercially produced silica spheres may stimulate experimental interest in this field. Still, some fundamental problems persist which require further investigation.

## ACKNOWLEDGMENTS

We would like to thank Dr. A. P. Philipse (University of Utrecht, The Netherlands), Dr. S. M. Underwood (RMIT, Melbourne, Australia), and Dr. K. Marquard (Merck GmbH, Darmstadt, Germany) for providing particle samples and for stimulating and helpful discussions on their properties. R123 was supplied by Solvay Fluor und Derivate GmbH (Hannover, Germany), and the paraffin oil ISO 15 by Zeller & Gmelin GmbH (Eislingen, Germany). Thanks are due to R. Krauss (University of Stuttgart, Germany) for making excerpts of the MIDAS database available and to M. Leucker and Dr. M. Moll for sample analysis. Part of the measurements were performed by A. Dubbert. Financial support for part of the work has been provided by the Deutsche Forschungsgemeinschaft.

## REFERENCES

1. W. A. Wakeham, A. Nagashima, and J. V. Sengers, eds., *Experimental Thermodynamics, Vol. III, Measurement of the Transport Properties of Fluids* (Blackwell, Oxford, 1991).
2. C. M. B. P. Oliveira and W. A. Wakeham, *Int. J. Thermophys.* **14**:1131 (1993).
3. Y. Tanaka and T. Sotani, Progress Report to the IEA Annex 18, in *Thermophysical Properties of the Environmentally Acceptable Refrigerants, Attachment 4* (Maastricht, 1993).
4. J. H. Dymond and H. A. Oye, *J. Phys. Chem. Ref. Data* **23**:41 (1994).
5. B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Krieger, Malabar, 1990).
6. B. E. Dahneke, ed., *Measurement of Suspended Particles by Quasi-Elastic Light Scattering* (Wiley, New York, 1984).

7. A. Leipertz, *Int. J. Thermophys.* **9**:897 (1988).
8. K. Kraft, S. Will, and A. Leipertz, *Measurement* **14**:135 (1994).
9. R. R. Brunson and C. H. Byers, *J. Chem. Eng. Data* **34**:46 (1989).
10. C. A. Herbst, H. E. King, Z. Gao, and H. D. Ou-Yang, *J. Appl. Phys.* **72**:838 (1992).
11. P. N. Pusey and W. van Megen, *J. Chem. Phys.* **80**:3513 (1984).
12. P. C. Hiemenz, *Principles of Colloid and Surface Chemistry* (Dekker, New York, 1986).
13. J. W. Jansen, C. G. de Kruif, and A. Vrij, *J. Colloid Interface. Sci.* **114**:471 (1986).
14. W. van Megen and S. M. Underwood, *Phys. Rev. E* **47**:248 (1993).
15. H. M. Fijnaut, C. Pathmamanoharan, E. A. Nieuwenhuis, and A. Vrij, *Chem. Phys. Lett.* **59**:351 (1978).
16. S. Will and A. Leipertz, *Appl. Opt.* **32**:3813 (1993).
17. D. E. Koppel, *J. Chem. Phys.* **57**:4814 (1972).
18. R. Krauss, *MIDAS Database for Thermphysical Properties* (Lehrstuhl für Technische Thermodynamik und Thermische Verfahrenstechnik, Universität Stuttgart).
19. P. W. Rouw, A. Vrij, and C. G. de Kruif, *Prog. Colloid Polym. Sci.* **76**:1 (1988).
20. A. P. Philipse and A. Vrij, *J. Colloid Interface Sci.* **128**:121 (1989).
21. *PTB Stoffdatenblätter, SDBI Aceton, Physikalisch Technische Bundesanstalt* (Braunschweig, Berlin, 1992), p. 4.
22. H. Bauer and G. Meerlender, *Rheol. Acta* **23**:514 (1984).
23. D. N. Petsev and N. D. Denkov, *J. Colloid Interface Sci.* **149**:329 (1992).
24. G. A. Schumacher and T. G. M. v. d. Ven, *J. Chem. Soc. Faraday Trans.* **87**:971 (1991).
25. E. Kuss, *Z. Angew. Phys.* **7**:372 (1955).