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The Quantitative Determination of the  
Composition of Liquids (Mixtures of  
several components), based on their  
Selective Absorption in the Infra-red  
Spectral Region

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Because of the importance of these substances for aeronautics, a rapid and correct method of characterising fluids - and to a great extent fuels also - has become urgently necessary. The present work is for the purpose of showing that selective transmission analysis in the infra-red spectral region can be used for investigating chemically pure fluids and mixtures. The measuring technique in use is described, and examples are given of how the quantitative composition of mixtures of two or three fluids can be found by a determination of the selective infra-red absorption.

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## I. INTRODUCTION

In connection with measurements of the selective absorption of gelatine in the infra-red spectral region, and with the intention of simplifying the often very complicated processes for analysing fluids, and above all of fuels, by using optical methods, the idea was mooted of using infra-red selective absorption analysis for investigating these substances. An infra-red monochromator of the Zeiss firm was set up, and calibrated, and a series of orientating measurements was made, which proved that this method was suitable for quantitative investigations of mixtures of two or three components.

## II. TESTS

### 1. The Installation

For investigating the selective infra-red absorption, the mirror monochromator of Zeiss, shown in Fig. 1a, which is distinguished by its compactness and the relatively high intensity of its light, was used. As the apparatus was intended mainly for use in investigations in the near ultra-red spectral region (about  $3\mu$ ), a quartz prism was used throughout.

Fig. 1a. Mirror monochromator of Zeiss  
(about  $\frac{1}{4}$  natural size). Casing open

Fig. 1b. Path of the rays in the mirror monochromator  
(diagrammatic representation).

The following is a brief description of the structure and method of working of the monochromator:-

A bundle of light rays which is omitted by a light source passes through a slit 1, and impinges on a concave mirror 2. The light is reflected from here in a parallel beam, through a plane mirror 3 on to a prism 4, where it is spectrally analysed. The light which passes on from here impinges on a second concave mirror, and from it a second spectrum is formed at the exit 6. The plane mirror 3 and the prism 4 are fastened together to a pivoting table. The pivoting of this table, which is connected with a tangential screw 9 via a fulcrum about 180 mm long, makes it possible to set any wave length selected. The replaceable prism requires a minimum of adjustment in each case in order to set the wave-length which is filtered through the exit gap. The tangent screw is so constructed as to allow the prism table to be adjusted with complete accuracy. It has also a drum, with 100 graduations marked on it. The entry and exit slits are symmetrical precision slits, and are fastened together and built into the cylindrical wall of the casing at an angle of  $122^\circ$ .

The following accessories were used for the measurements in the infra-red and visible spectral regions.

- (a) A thermo-couple with a heat-insulating plate, Zeiss pattern (Fig. 2) as a receiver for the rays
- (b) A linear vacuum thermo-couple made by the firm of Muller (Fig. 3)
- (c) A Zeiss loop galvanomotor (Fig. 4)
- (d) Light source with optical instruments and cell-holder (Fig. 5)

## 2. Testing the Installation

Before beginning the actual investigations it was necessary to calibrate the mirror monochromator; that is, to allocate a wave-length for the monochromatic radiation leaving the exit slit, to each setting of the drum. These measurements, as far as the visible spectral range is concerned, were made at DVL with the aid of mercury and rubidium lamps. The calibration of the infra-red spectral range, which could not be carried out at DVL for want of a suitable device, was very kindly done by Oberregierungsrat Dr. Wetthauer of the Reich Physical-Technical Institute with a monochromator of the P.T.R. The results of the measurements are given in the calibration curve (Fig. 6), which shows the wave-length allocated to the different divisions of the drum for the radiation leaving the exit slit of the infra-red monochromator.

Also, the thermo-couple shown under Ia was thoroughly checked. The thermo-current generated by the impinging of the ray was measured by the galvanometer shown in Ic. The sensitivity of this aperiodic loop galvanometer is about  $7.5 \cdot 10^{-9} \text{ A.}$  per division of the scale when the loop is vertical. For greater convenience in reading, the deflection of the loop is observed through an optical instrument with 650 fold magnification. Investigations which were made later showed that the sensitivity of this type of loop galvanometer was adequate, although for precision measurements and especially for very small thermal forces or deflections a more sensitive mirror galvanometer was preferable.

When the thermo-couple supplied by the firm of Zeiss was tested, it appeared at first that the thermo-pile did not possess the maximum sensitivity which was required. It was therefore replaced by a thermo-loop in a high vacuum, in a cylindrical sheath, which is for the purpose of increasing the sensitivity. On the basis of the experiences which the firm of Muller, Zehlendorf, gained in manufacturing their thermo-element, DVL produced a linear thermo-couple, type Fh<sub>2</sub> (Fig. 3). This is a thermo-couple with increased impact resistance in a cylindrical glass mantle with 2 plane quartz glass windows which are melted in, opposite to each other, for the purpose of better adjustment. The thermo-couple has a specially sensitive long, narrow receiving strip.

When this accessory was compared with the radiation receiver developed by Zeiss, it appeared that the maximum gain in sensitivity was in the region of 20-25%. On the other hand, further very complicated accessories were required for attaching it to the mirror monochromator and the source of radiation. Therefore, in view of the experiences gained from testing the two installations, the Zeiss thermo-couple continued to be used.

## 3. Materials Investigated

For investigating the selective absorption in the infra-red spectral region, and in the later tests with the new measuring technique, chemically pure substances were generally used. They can be seen in the diagram in Fig. 7. In addition to these fluids, the following were also used: gasoline, benzene, hexane, heptane and pentane; also arbitrary mixtures of chemically pure substances and fuels. As a fuel with an additive, a leaded gasoline was used. This gasoline, which is known as B4, has already been used in aviation and has proved its value. Apart from this, aero-engine fuels were used.

Fig. 8. Optical device for passing parallel rays of light through a measuring cell. (diagrammatic)

Since it is assumed that the chemical structure and the physical data of the chemically pure substances and the fuels are sufficiently well known, it is possible in this report, which only touches on the investigation of the multi-component mixtures, to refrain from discussing in detail the single, double and multi-component mixtures. It also appears superfluous to give the figures which are the basis of the diagram in the form of tables.

4. Selective transmission curves in the infra-red spectral range as a function of the temperature of the liquid measured and the position of the measuring bulb in the path of the rays

The percentual selective transmission curves in the infra-red spectral range were measured for a series of fluids with the cells containing the liquids in the path of parallel rays (Fig. 8), before the entrance slit of the monochromator. The deflection of the loop galvanometer was measured at definite wave-length intervals with an empty cell in the path of the radiations (galvanometer deflection or intensity =  $I_0$ ), and with a filled cell (galvanometer deflection or intensity =  $I$ ). The percentual selective transmission was found to be

$$D_{\lambda} = \frac{I}{I_0} \cdot 100$$

The percentual absorption curves found in this way for a series of substances with a layer of 10 mm thickness are shown in Figs. 9 to 17. The substances whose selective absorption curves are shown in Figs. 9 to 15 have been investigated elsewhere<sup>1) 2)</sup>.

But the curves in 16 and 17, which refer to lubricating oils as well as to mixtures of fuels, are published for the first time in this work. As regards all the curves (see Figs. 9 to 17), it must be mentioned that by improving the accuracy of measurement (finer slit, shorter wave-length intervals, more sensitive thermocouple), the accuracy can be still further improved as regards the fine structure of the curves.

The selective transmission curves in Figs. 9 to 18 were made, as already mentioned, with the cell carrier before the entry slit of the monochromator. The results changed gradually and steadily when the measurements were repeated several times, using the same fluid with the source of radiation permanently switched on. This is easily explained by the fact that when the measuring cell is fitted before the entry slit the whole of the undecomposed light penetrates the medium which is being measured, with the result that the temperature of the liquid being measured increases and its selective transmission is altered.

Figs. 9 and 13. Selective absorption curves of various substances

In order to show clearly that the selective transmission is a function of the temperature of the absorbing medium, a cell

1) Landolt Bornstein, phys-chem. Tables

2) E. Frabert & K. Schaum, Absorption spectra of hydrocarbons and halogen derivatives in the near ultra-red band. Zeitschrift für Wissenschaftliche Photographie, Vol. 35, H.7, July 1936

filled with gasoline, with a temperature at one time of 20°C and at another time of 50°, was introduced into the path of the parallel rays before the entry slit of the monochromator, and for simplicity's sake the spectral intensity curve was determined. Fig. 18 shows that the form of the spectral intensity curve, and thus the selective absorption, is a function of the temperature of the absorbing medium. This proves that in carrying out measurements the constancy of the temperature of the absorbing medium requires attention.

Since, with the bulb before the entry slit of the monochromator considerable additional apparatus is required to keep the temperature constant, it appeared a good idea to arrange the cells behind the exit slit of the monochromator, as has been done elsewhere in different investigations. The advantage of the last arrangement is that, in place of the undecomposed total light (bulb before the entry slit), in this case only the low monochromator radiation which leaves the exit slit penetrates the fluid being measured, so that the latter undergoes a minimum of heating.

Therefore, in all the investigations which followed, the cells with the fluid to be investigated were placed behind the exit slit of the monochromator, thus making manipulation easier.

Fig. 14. Selective transmission curve of ethyl alcohol

Fig. 15. Selective transmission curves of hexane, pentane, and leaded gasoline.

## 5. A rapid method for characterising a material and the proportion of it in mixtures

### (a) Description of the Method

In the determination of percentual selective transmission curves, the principle was that, at certain wave length intervals, the galvanometer deflection was measured once ( $I_0$ ), with the cell empty and once ( $I$ ) with the cell charged with fluid. The proportion was obtained by calculation by multiplying  $\frac{I}{I_0}$  by 100. When the apparatus is ready for

working, all the experimental work required is the fixing of a measuring point on the transmission curve from two measurements. Now, since, in order to plot a complete selective transmission curve such measurements must be made for a large number of points in the spectrum, much labour would be saved if the number of measurements could be reduced, without reducing the number of measuring points from which the final curve is plotted. But this is obviously possible if the percentual selective absorption curves are not determined, but, instead of the

$$P\% = 100 \frac{I}{I_0}$$

values, only the  $I$  values are determined. This means that if the strength of the radiations is kept constant the deflections of the galvanometer are determined only for a series of points in the spectrum, the cell with the liquid under test being between the outlet slit of the monochromator and the thermocouple. The curves so obtained, which require only half the experimental time, will henceforth be called "intensity curves" or "relative transmission curves". The curve so obtained is not only a function of the selective absorption of the substance measured, but also of the distribution of the spectral energy which prevails at the exit slit of the monochromator. Also, when the measuring cells were behind the exit slit no

account was taken of the fact that the rays penetrate the bulb parallel to each other, so that the curves plotted by the rapid method are also a function of the size of the selective refractive index of the liquid. The following description will show that the quantitative composition of fluids can be determined swiftly and with sufficient accuracy by finding the I-values, partly for a definite wave length, partly for several wave-lengths.

Fig. 16. Selective transmission curves of various lubricating oils

Fig. 17. Selective transmission curves of gasoline, benzene, and their mixtures.

Fig. 18. Influence of the Temperature on the shape of the selective transmission curves.

(b) Investigation of various liquids and of arbitrary mixtures of liquids, especially fuel mixtures

First, the relative transmission of a series of chemically pure liquids was investigated in the infra-red spectral region at a constant wave-length ( $\lambda = 1775 \text{ m}\mu$ ). Thus, for simplicity's sake the galvanometer deflections at constant intensity of radiation were found with the bulbs containing the liquids behind the exit slit of the monochromator. These tests, the results of which are shown in Fig. 7, prove that the substances investigated, which are practically colourless in the visible region are - as regards their relative infra-red transmission - more or less different from each other. There is no doubt that the relationship between the relative transmission of two substances in the infra-red region of radiation changes from wave-length to wave-length. This is clearly seen from the spectral intensity curves of the same pure substances (see Fig. 19).

Fig. 19. Spectral intensity curves of various chemically pure liquids and fuels

On the basis of this experimental data, the following may be stated about the methods and the amount of work involved in determining the quantitative composition of a liquid made up of two different components.

(a) If the relative transmission curve for a certain infra-red wave-length, which gives the relative transmission of a mixture of two components as a function of the proportion per cent of one of the components, shows neither a maximum nor a minimum when the path of the curve is continuous, then by means of a calibration curve the quantitative composition of a mixture of unknown proportions can be determined on the basis of a single galvanometer deflection.

The range of application of the rapid method can be illustrated by two examples:-

The curves in Figs. 20 and 21 show the relative absorption of an alcohol-carbon tetrachloride mixture as a function of the carbon tetrachloride content and of an alcohol-acetone mixture as a function of the acetone content at a constant wave-length ( $\lambda = 1775 \text{ m}\mu$ ).

The determination of the quantitative composition of an alcohol-carbon tetrachloride mixture or of an alcohol-acetone mixture by the optical rapid method requires only one measurement of the galvanometer deflection with the above calibration curve, if, at a definite intensity of the radiation the cell containing the solution to be investigated is behind

the exit slit of the monochromator and the drum is set to the wave-length which is allocated to the calibration curves. After the galvanometer deflection has been determined, the quantitative composition of the mixture can be read off from the test diagram. The accuracy of the method is equal to that of chemical analysis.

(b) If the curves described under (a) show a minimum or a maximum, two calibration curves for two different wave-lengths as far as possible with different shapes are required for the quantitative determination of the composition of a two-component mixture. The determination of the quantitative composition of two-component mixtures on the basis of two calibration curves for two different wave-lengths and two measurements (galvanometer deflections) is illustrated by the case of a gasoline-benzene mixture. Suppose the curves are known for the gasoline-benzene mixture, which show the relative transmission of a gasoline-benzene mixture as a function of the benzene content for infra-red rays of the wave-lengths  $\lambda = 1775 \text{ m}\mu$  and  $\lambda = 1650 \text{ m}\mu$  (see Fig. 22)

Fig. 20. Relative absorption of an alcohol-carbon tetrachloride mixture as a function of the carbon tetrachloride content at constant wave-length ( $\lambda = 1775 \text{ m}\mu$ )

Fig. 21. Relative absorption of an alcohol-acetone mixture as a function of the acetone content at constant wave-length ( $\lambda = 1775 \text{ m}\mu$ )

Fig. 22. Relative absorption of a gasoline-benzene mixture as a function of the benzene content at different wave-lengths ( $\lambda = 1775 \text{ m}\mu$  and  $\lambda = 1650 \text{ m}\mu$ ).

Fig. 23. Relative absorption of a gasoline-benzene mixture as a function of the benzene content at various wave-lengths.

Fig. 24. Extract from Fig. 23. Calibration curves without the criteria of maxima and minima.

If the mixture to be investigated consists of 80 parts of gasoline and 20 parts of benzene, then if the charged cell is behind the exit slit of the monochromator and  $\lambda = 1650 \text{ m}\mu$ , the galvanometer deflection (intensity) is equal to 58 divisions of the scale. It was impossible to decide from this single measurement whether the mixture was of 80/20 gasoline-benzene or of 20/80 gasoline-benzene.

We therefore measure the absorption of the mixture a second time, using the wave-length  $\lambda = 1775 \text{ m}\mu$ . The galvanometer deflection of 17 divisions means that (neglecting the first curve) the mixture can be of 80/20 or 60/40. As the ratio 20/80 is true of both curves, the mixture could only be of gasoline and benzene in the ratio 80/20.

If one plots a series of calibration curves for a two-components system, for various infra-red  $\lambda$  values, those curves showing the relative transmission as a function of the proportion per cent of a component in a two-component mixture at constant wave-length, part of a calibration curve has a maximum or minimum, while another part will not have those criteria (Figs. 23 and 24).

Therefore, when carrying out current investigations into the composition of two-component mixtures, it will be as well



to plot calibrating curves first for various  $\lambda$  values, so that if it should turn out later that there were maxima and minima among the calibrating curves, only these will be used.

Of course, the measurements described can also be made by entering  $I_0$  instead of  $I$ -values when plotting the calibrating curves. Although such calibrating curves have a different form from the ones obtained, the method of evaluation remains the same, and so leads to the same results. Calibrating curves of the latter type can well be used when there is difficulty in keeping the temperature of the radiations constant, or if there is danger of errors in adjustment when the radiation is projected at the entry slit of the monochromator.

Whereas the quantitative composition of any two-component mixture can be determined in the way described rapidly, and with an accuracy at least as good as that of one of the long-drawn-out chemical analyses, its range of application is more limited owing to the increasing difficulties which arise with multi-component mixtures. The simplest case is that in which the proportion per cent of a component in a three-component mixture is known, or can be found rapidly by analysis (titration, distillation, etc.)

Fig. 25. Spectral intensity curves for a series of solutions of a three-component mixture of carbon tetrachloride (10%)-acetone-ethyl alcohol with the components in various ratios

Fig. 26. Spectral intensity curves for a series of solutions of the three-component mixture carbon tetrachloride (30%)-acetone-ethyl alcohol, with the components in various ratios.

Fig. 27. Spectral intensity curves for a series of solutions of the three-component mixture carbon tetrachloride (50%)-acetone-ethyl alcohol with the components in different ratios.

In this case the problem and its solution consist in the investigation of a two-component mixture (see cases (a) and (b)). This means that three-component test solutions will be produced in which the proportion of one of the components (the one which is most easy to determine analytically) agrees with the proportion of this component in the three-component mixture. The individual test solutions will differ only as regards the proportions of the other two components, if one of the proportions is constant. On the basis of one, or two, calibration curves, in which the galvanometer deflection at a given wave-length appears as a function of the ratio in which the second or third components are present when the proportion of the first component is constant, the quantitative composition of a three-component mixture can be determined by means of a measurement of transmission for a definite wave-length (case (a)), or by means of two absorption measurements at two different wave-lengths (case (b)).

More work is involved when the quantitative composition of a three-component mixture is determined optically, that is, when it is not possible to determine one of the components chemically. In this case, it is necessary to plot the infra-red spectral intensity curves for a series of solutions with the components in various ratios, as, for example, in the carbon tetrachloride-acetone-alcohol mixture of Figs. 25 and 26. There is thus a series of families of curves, which correspond to a



constant proportion of one component and various proportions of the other components, altering according to the proportions of the other two components. In order to determine the quantitative composition of an unknown mixture of three components it is necessary, after plotting the spectral intensity curve, to determine between which test curves this curve runs. This gives, in the first place, the rough composition of the unknown three-component mixture, and must be followed by a more exact determination through graphic interpolation.

The investigations which were carried out show how two and three-component mixtures can be tested quantitatively by determining their infra-red relative absorption. The examples make it clear that two-component mixtures can be analysed rapidly with a minimum of effort and sufficient accuracy. It also appeared that, naturally with great labour, three-component mixtures can be determined optically. It is to be expected that as the number of components increases the difficulties of quantitative determination will also increase. Whether, in view of these facts, it is possible to determine multi-component mixtures with sufficient accuracy (lubricating oils, Diesel fuels; etc.), can only be decided by numerous tests, in which it is possible that an even greater infra-red spectral range will have to be used (e.g. from 1 to 15  $\mu$ ).

### III. SUMMARY

After investigating the dependence of the selective transmission curves in the infra-red spectral range on the temperature of the liquids measured and on the position of the measuring all in the path of the rays, the measuring process was discussed. After it had proved that a series of colourless fluids have differing absorption for a certain type of infra-red radiation, the manner in which the quantitative composition of two-component mixtures can be determined from test-curves was demonstrated. Examples were also given of how the composition of a three-component mixture can be determined optically if the proportion per cent of one of the components is known. In conclusion, a description is given of how the composition of a mixture of three known components can be ascertained without chemical analysis from the selective infra-red transmission curves.