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The influence of conductivity on the Karl Fischer titration

S. Grünke*

Merck KGaA, Analytics & Reagents , 64271 Darmstadt, Germany

Abstract

The Karl Fischer titration is indicated voltametrically or amperometrically by polarising a double platinum electrode. The endpoint is recognised by a strong decrease of the resistance of the solution, caused by a small excess of iodine molecules. A minimum conductivity of the KF solutions is necessary for indicating the endpoint. In conventional methanolic Karl Fischer solutions, dissolved components assure a sufficient conductivity. But substitution of methanol by less polar solvents can lead to indication problems. The relationship between conductivity and indication for various volumetric one-and two-component systems is shown.

For the coulometric method, the conductivity of KF solutions is of especial importance. The generation of iodine at the cathode requires a higher conductivity than is necessary for indicating the endpoint. The aim of further developments is to adjust new reagent compositions to standard parameters of the instrument. Some examples of new Karl Fischer solvents are given.

Keywords: Karl Fischer titration; Indication of endpoint; Conductivity of Karl Fischer solutions

1. Introduction

1.1. General

Water determinations according to Karl Fischer (KF) are based on a redox reaction, where sulphur dioxide (SO_2) is oxidised by iodine (I_2) in the presence of water. Water is determined as a stoichiometric reaction partner.

The main reaction can be simply described by a two-step mechanism (Cedergren, 1974; Scholz, 1984; Verhoef, & Barendrecht, 1976). In the first step, alkyl sulphite is formed, when dissolving sulphur dioxide in alcohol [Eq. (1)]. In the second step, alkyl sulphite is oxidised by iodine, where water is involved [Eq. (2)].

$$\mathrm{ROH + SO_2 + RN \rightleftharpoons [RNH]SO_3R} \quad (1)$$

$$\mathrm{[RNH]SO_3R + I_2/I_3^- + H_2O + 2\ RN \rightarrow [RNH]SO_4R + 2[RNH]I} \quad (2)$$

R-alkyl group, RN-base

According to the latest results, it is now known, that the reactions occurring in Karl Fischer solutions are more complex than assumed (Grünke, 2001). In dependence of the reaction conditions, various equilibria do compete. In addition to alkyl sulphite, hydrogen sulphite can be formed in alcoholic solutions containing SO_2. HSO_3^- is also oxidised by iodine. This oxidation proceeds via the liberation of SO_3, which further reacts with the nucleophilic components in the KF solution (water, base and alcohol) (Fischer, Beil, & Krenn, 1992).

Generally, KF solutions are based on four main components: iodine, sulphur dioxide, base and solvent. Iodine and sulphur dioxide are necessary for the KF reaction and cannot be replaced. The task of the base is buffering the pH of the KF solution in the optimum range between 5 and 8. The formerly used pyridine is nowadays almost completely replaced by alternative bases, such as imidazole or diethanolamine.

The solvent determines the stoichiometry and the rate of the KF reaction, since it takes part in the mechanism itself. Furthermore, the solvent determines the dissolving capacity of the KF solution. In order to reach optimum KF conditions a reactive and polar alcohol is necessary. Therefore the KF-titration is still widely based on the use of methanol. In methanol a fast reaction and an accurate 1:1 (I_2:H_2O) stoichiometry is obtained. Methanol is also a suitable solvent for a variety of samples. If dissolving problems occur, other solvents, such as long chain alcohols, toluene, chloroform or formamide, can be added.

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* Tel.: +49-61-51-72-98-49; fax: +49-61-51-72-919849.
E-mail address: silke.gruenke@merck.de (S. Grünke).

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Despite methanol being the most suitable solvent for KF titration, there have always been tendencies to find alternative solvents. Thus, for the determination of aldehydes and ketones, methanol-free reagents were developed in order to suppress or reduce side reactions. Methanol has also been completely replaced in one-component reagents. In order to obtain stable one-component reagents, less reactive alcohols have to be chosen as solvent. Nowadays, diethylene glycol monoethylether is used for this purpose.

Latest developments aim to find alternative solvents for methanol because of its toxic properties. Here the use of ethanol or 1-propanol is obvious, but not as simple as supposed.

If pure ethanol or propanol, instead of methanol, is used as the solvent for titrations with one-component reagents, a dark coloured solution is often observed at the endpoint, indicating a larger excess of iodine than in methanol. The tendency of overtitration strongly increases with each titration and less reproducible results are obtained.

What are the reasons for this behaviour? It is known that, in long-chain alcohols, a decreasing reaction rate of the KF reaction is measured with increasing chain length of the solvent (Grünke & Wünsch, 2000). But since the KF reaction is still a fast reaction, the kinetic aspect cannot be recognised as the main reason for the observed overtitration. After studying the behaviour of KF solutions based on 1-propanol, it was found, that problems of overtitration were more related to indication problems.

1.2. Indication of KF titration

The endpoint of the KF titration is indicated voltametrically or amperometrically by polarising a double platinum electrode. A constant polarising current is set when performing voltametric measurements. Here the voltage between the platinum pins is measured in dependence of the added volume of titrant. The measurement of the current at a fixed polarising voltage is a less common mode of operation. As long as traces of water are present in the titration cell, all iodine molecules are immediately reduced to iodide by the KF reaction. The electrical resistance of the solution stays at a high level. After titrating all water molecules, a small excess of iodine molecules leads to a strong decrease of the resistance of the solution, caused by cathodic reduction of I_2/I_3^- and anodic oxidation of I^-.

It is known that the type of solvent influences the indication of the endpoint. So the electrochemical behaviour of KF solutions is determined by the standard electrode potential of the redox couple I_2/I^- ($E(I_2/I^-)$). $E(I_2/I^-)$ is a characteristic constant for each solvent, independent of the composition of KF solutions. If, in solutions with different iodine concentrations, the voltage is measured in dependence of the polarising current, the optimum ranges of the parameters I and E can be determined from the resulting functions. In methanolic KF solutions, optimum conditions for indicating the endpoint were obtained with $I_{pol} = 5–100$ μA and $E_{stop} = 50–600$ mV (Wünsch & Schöffski, 1991). But in 1-propanol, I–E curves increase already at a lower current than in methanol at the same iodine concentrations (Fig. 1). This is due to the decreasing standard electrode potential of I_2/I^- in long chain alcohols in comparison to methanol (e.g. $E(I_2/I^-$, methanol$) = 0{,}357$ V, $E(I_2/I^-$, ethanol$) = 0.305$ V). Therefore, a higher excess of iodine is produced at the endpoint, if the titration in 1-propanol is performed with the same parameters as in methanol (Wünsch & Grünke, 1998).

In principle, a higher excess of iodine does not inevitably lead to problems as long as reproducible iodine concentrations are produced. But when the excess necessary to reach the conditions of the endpoint (stop voltage) increases, the risk of non-reproducible overtitration increases too. Finally the titrator cannot stop the dosage of iodine.

In addition to the standard electrode potential, the optimum stop voltage is influenced by the conductivity of the solution, which is determined by the type of solvent and the solved components. According to Guinon, Grima, and Garcia-Anton (1991) the dielectric constant and the viscosity of solutions have a direct effect.

As a result of the earlier investigations, it was concluded, that the titration parameters, I and E, have to be adjusted to the solvent. For example, reproducible results were obtained in 1-propanol by lowering I_{pol} in a range between 5 and 25 μA (Wünsch & Grünke, 1998).

But, for the user of the KF titration, it is more convenient to work with the standard parameters of the instrument. Therefore, development activities in the field of KF reagents aim at adjusting the composition of the reagents in a way that a change of the parameters may not be necessary.

The influence of the type of Pt-electrode and the mode of controlling current/voltage is not considered in this paper.

In this study, the importance of conductivity for the volumetric and the coulometric methods is shown. In the field of volumetry, various one-and-two component systems are compared.

2. Materials and methods

2.1. Instruments

For measurements of conductivity were with a Qcond 2400.

KF instruments were KF titrator DL 38 (Mettler), 756 KF coulometer (Metrohm)

Reagents (all Merck KGaA) were, for one-component titration: KF reagent with pyridine (item 109248), KF reagent 5 (item 109234), apura CombiTitrant 5 (item 188005), methanol (item 106009), chloroform (item 102445), ethanol (item 108060), diethylene glycol monoethylether (item 803127), toluene (item 108325), apura CombiSolvent (item 188008) and for two-component titration: apura Titrant 5 (item 188010), apura Solvent (item 188015), home-made ethanolic titrant and solvent with comparable composition, and for coulometric measurements: apura CombiCoulomat fritless (109257).

In first test series, the course of conductivity during one-component and two-component titrations with various titrants and solvents was measured according to the following procedure: 60 ml solvent were filled into the titration cell and 50 μl water were added. While stirring, 10 ml of titrant solution were added in steps of 0.25 ml or 0.5 ml. After each step a reading of the adjusted conductivity was taken.

3. Results and discussions

3.1. Comparison of the course of conductivity for various one component systems

One component reagents contain all reactive components (SO_2, I_2 and base) necessary for the KF reaction in one solution. A reactive alcohol, preferably methanol, or a solvent mixture corresponding to the properties of the sample, is chosen as solvent in the titration cell. In solvent mixtures, a minimum content of reactive alcohol, between 30 and 50%, is necessary, in order to ensure the proceeding of the KF reaction and to prevent interferences by the Bunsen reaction leading to deviations of the 1:1 stoichiometry.

At the beginning of the one-component titration, a low titration rate is observed. Particularly with solvent mixtures containing nonpolar solvents, such as toluene or xylene, pretitration takes a long time. But after adding a few millilitres of titrant solution, the titration approaches a constant rate.

The reason for this behaviour is that the fresh solvent in the titration cell contains no reaction components apart from the alcohol. With the addition of titrant solution and increasing concentration of reactants in the titration cell, the reaction rate increases. Besides the kinetic aspect, it has to be considered, that the fresh (pure) solvent is a non-conductor. With pretitration, ions are added and the conductivity of the solution increases.

The course of conductivity, during one component titration with three different reagents and several solvents, was followed. Figs. 2 and 3 show that there is no linear increase of conductivity with concentration. Molecular interactions between ions lead to curved functions.

When comparing various one-component titrations with methanol in Fig. 2, the influence of the composition of one-component reagents is reflected. The courses of conductivity for CombiTitrant 5 (188005) and the pyridine-containing KF reagent (109248) are comparable, despite their different compositions. CombiTitrant 5 is based on the low polar diethylene glycolmonoethylether and imidazole. KF reagent (109248) contains the more polar 2-methoxyethanol as solvent and pyridine, corresponding to the conventional reagent described in

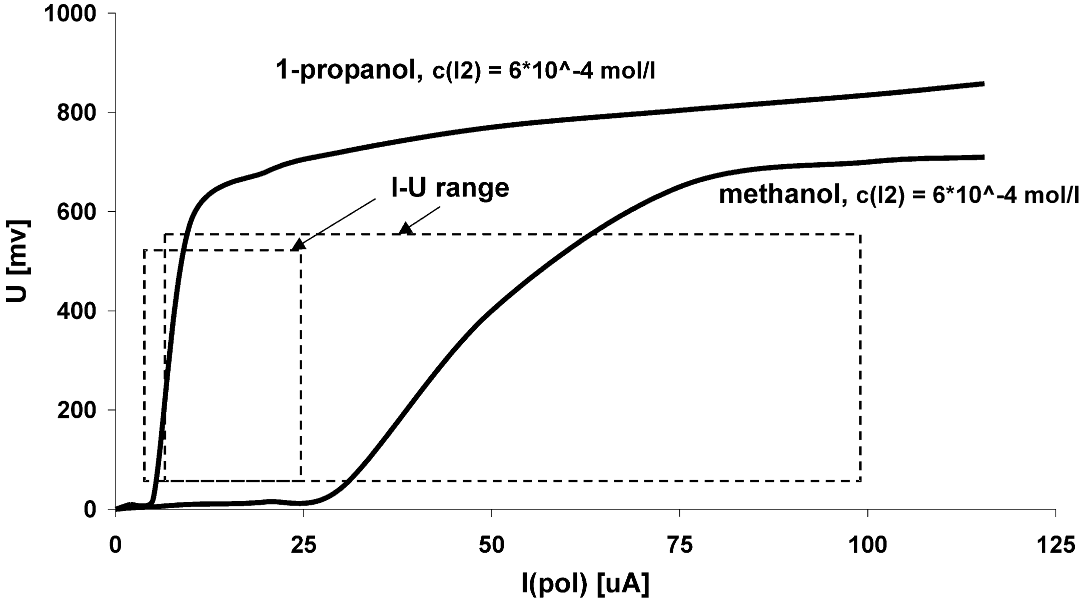

Fig. 1. Isoiodales in methanolic and propanolic KF solvent (1.2 mol/l SO_2, 1.8 mol/l imidazole, 0.1 mol/l iodide). The marked regions correspond to the optimum working ranges for KF titrations in methanol and propanol (Wünsch & Grünke, 1998; Wünsch & Schöffski, 1991).

the European Pharmacopoeia (European Pharmacopoeia Commission, 2002). With KF reagent (109234), the conductivity during the titration is lowered by a factor of 2. This reagent is based on the same solvent, DEGEE, like CombiTitrant 5, but differs in the type of base, which is here a special alkylated pyridine derivative of relatively high molecular weight.

In practical KF titration, KF reagent (109234) is known as less robust in combination with solvent mixtures of low polarity than the KF reagent (109248) or CombiTitrant 5. So, overtitration can occur with (109234) and solvent mixtures with toluene, when the methanol content in the titration cell is below 50%. The lower polarity and the lower conductivity of this one component reagent are regarded as the main reasons for this behaviour.

The influence of the type of solvent in the titration cell, during one-component titration with CombiTitrant

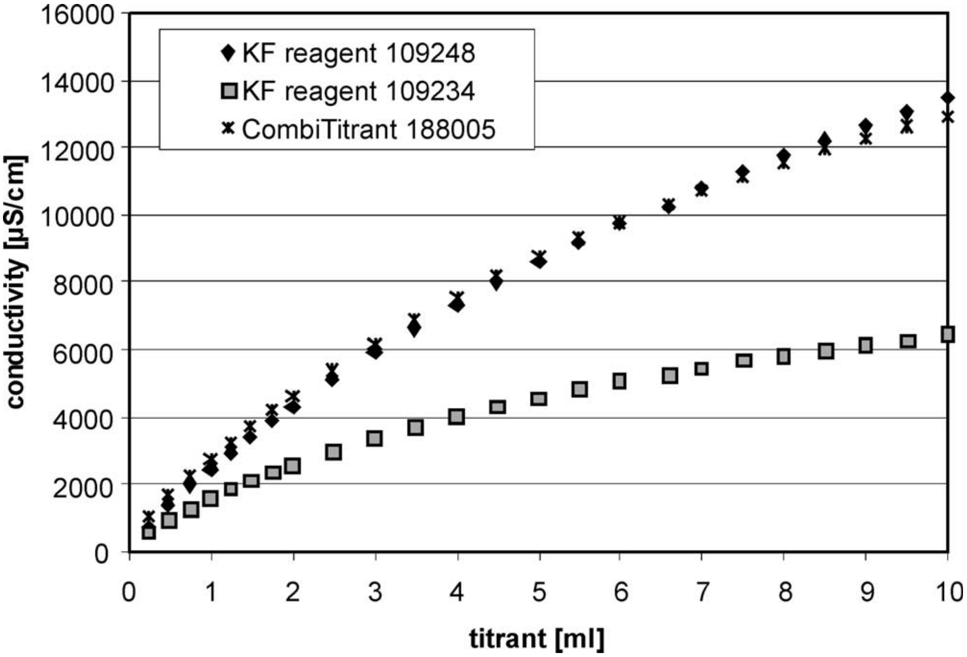

Fig. 2. Course of conductivity for KF titration with various one-component reagents and methanol as solvent.

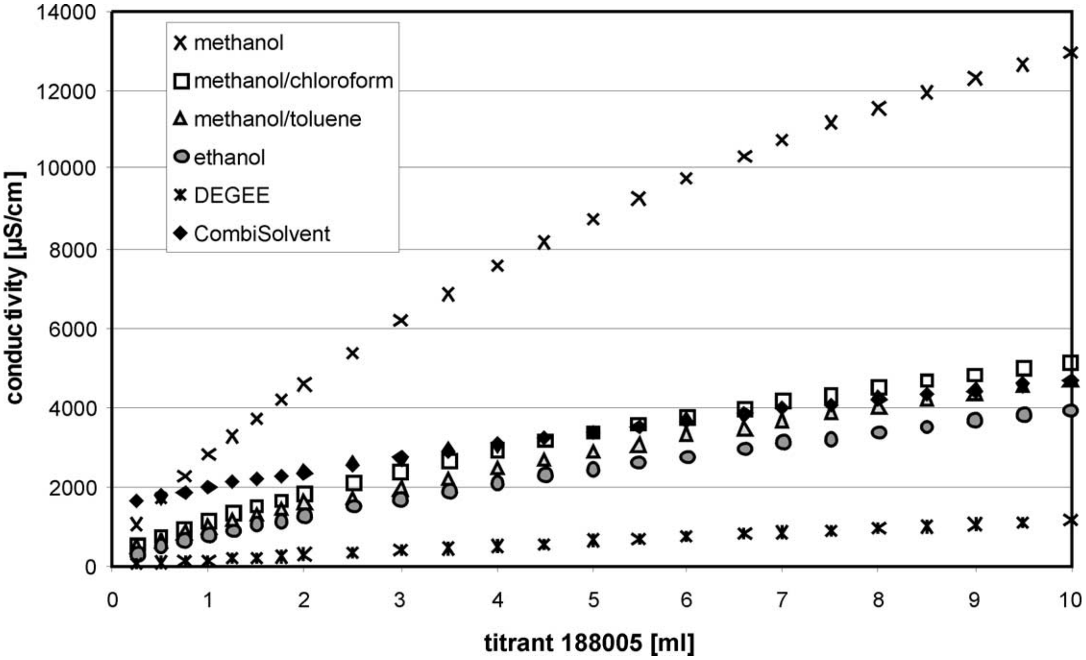

Fig. 3. Course of conductivity for titration with apura CombiTitrant 5 and several solvents.

5, is shown in Fig. 3. As expected, in methanol the conductivity increases the strongest. In mixtures with 50% methanol and 50% chloroform or toluene the conductivity is already lowered by a factor of 2.5 or 2.8. When methanol is completely replaced by ethanol, values decrease by a factor of 3. In praxis, the KF titration can be performed with these solvents, but tendencies to overtitration and indication problems could occur. By adjusting the titration parameters, the indication of titration can be optimised.

With DEGEE instead of methanol, the conductivity decreases by a factor of 10. In this range, the KF titration is not longer possible. Despite setting of different instrument parameters, the KF titrator constantly doses iodine, while the conditions of the endpoint are not fulfilled.

3.2. Course of conductivity for two-component titration in methanol and ethanol-based reagents

In two-component reagents, reactive components are separated into two solutions. The titrant component is based on iodine dissolved in a suitable solvent, preferably methanol. The solvent component contains SO_2 and a base dissolved in an alcohol.

The reactive components dissolved in KF solvents ensure optimum conditions from the beginning of titration. Both, a high reaction rate and an adequate conductivity enable a fast titration rate.

Fig. 4 shows, that the two component titration already starts at a high level of conductivity. During the titration, almost no change or increase of conductivity is observed.

With the methanolic two-component system, 28 mS/cm are measured. With the home-made ethanolic reagent, conductivity is lowered by the factor 3–9 mS/cm. In comparison to one-component titration, values of 13 mS/cm with methanol or 4 mS/cm with ethanol are reached after adding 10 ml of CombiTitrant 5.

KF titration with the home-made ethanolic system could be performed without problems, indicating a sufficient conductivity of this KF solution.

3.3. Consequences for volumetric KF titration

The earlier comparisons demonstrate the importance of conductivity for one and two component titrations.

One-component titrations are characterised by low initial conductivities and increased values with addition of reagent. In combination with methanol as solvent component, optimum conditions for indicating the endpoint are guaranteed, independent of the type of the one-component reagent. But, with decreasing polarity of the solution in the titration cell, the conductivity gains importance. Hence the polarity and conductivity of one-component reagents have to be considered. For example ASTM D 4377 describes the use of a one-component reagent in combination with a methanol/chloroform mixture (1/3) for water determinations in oils (ASTM D 4377, 2000). But, in dependence of the composition of the KF reagent, the user can face overtitration and indication problems.

For two-component systems, the course of conductivity during KF titration is determined by the dissolved SO_2 and base in the solvent component. Thus,

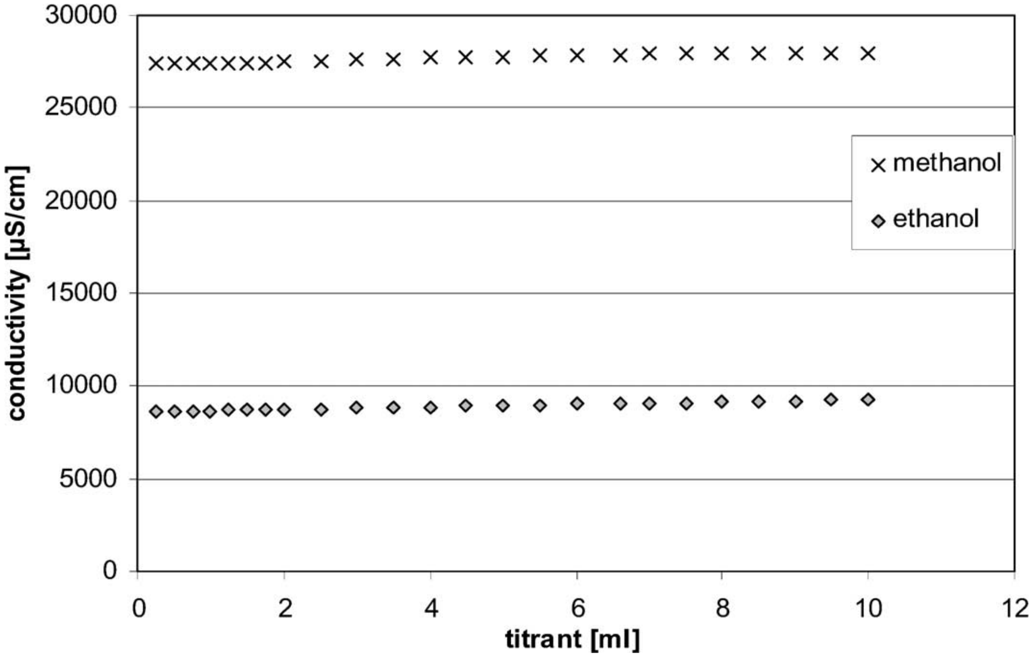

Fig. 4. Course of conductivity for titration with two component reagents based on methanol and ethanol.

optimum conditions are given from the start of titration. But by replacing methanol with less polar solvents, the conductivity decreases significantly and similar problems to these described for one component titration arise: low titration rate, sluggish endpoints and overtitration.

Another negative side-effect of low conductivity of KF solutions is the increased tendency toward coating of the electrode by dissolved salts of the KF reagent or by the sample. This effect also contributes to disturbances of indication and overtitration.

Indication problems, occurring after partial or complete replacement of methanol in KF reagents and caused by low conductivity and low electrode potential $E(I_2/I^-)$ in these mixtures, can be reduced or avoided by the adjustment of the instrument parameters. So, it is recommended to lower the polarising current and/or to increase the stop voltage at the endpoint.

In some cases it is also possible to work at increased titration temperatures, in order to reach a higher conductivity and at the same time a higher solubility of samples. For example, two-component titration in 1-propanol was performed with reproducible results at 80 °C (Wünsch & Grünke, 1998).

As an alternative to setting up different instrument parameters for different KF systems, the composition of KF solutions can be adjusted. The aim of our development activities was to increase the conductivity of solvents, in order to work with standard parameters of the instrument. For one component titration with less polar solvent mixtures, it was found that an initial value of 1 mS/cm is already advantageous. After adding 10 ml of one-component titrant, the conductivity should exceed 3 mS/cm.

This condition can be realised by adding salts to solvents in the titration cell. Suitable are various halides of organic bases. A more elegant and at the same time simpler opportunity to increase the conductivity of solvents for one-component titration is to add low concentrations of SO_2 and base. In this way, "diluted" KF solvents are obtained. The acceleration of the reaction rate at the beginning of titration is a positive side-effect, leading to faster pretitration and sample titration with a fresh solvent.

Thus a special solvent for one component titration, based on ethanol, was developed, after some indication problems with pure ethanol were observed (Fig. 3). By adding small concentrations of SO_2 and base, an initial conductivity of app. 2 mS/cm was adjusted, which is sufficient to overcome the indication problems. With this "diluted" KF solvent (apura CombiSolvent) a non-toxic alternative for methanol is available.

This experience is also used for the development of new solvents for one component titrations of oils and fats: apura CombiSolvent oils (item 188020) and apura CombiSolvent fats (item 188021).

CombiSolvent oil contains methanol and toluene and is especially recommended for mineral oils (e.g. raw oil). CombiSolvent fats is based on a solvent mixture of methanol, alkyl acetate and decanol and was developed as special solvent for fats based on esters for the food and cosmetics industries (e.g. margarine, peanut oil).

As mentioned previously, with the addition of less polar solvents, such as toluene or long chain alcohols to methanol, the course of conductivity during one-component titration decreases strongly and the influence on indication has to be considered. But by addition of small concentrations of SO_2 and base, the initial conductivity of the mixtures increases and leads to significantly shorter durations of pretitrations. Overtitration is prevented.

In a similar way the composition of two-component reagents has to be adjusted, when methanol is replaced by less polar alcohols. In conditions of sufficient conductivity, standard parameters of the instrument can also be used in systems based on ethanol or propanol.

For example, overtitration was observed with an ethanolic reagent of a conductivity of 4 mS/cm. KF titration was only possible after a lower I_{pol} (10 instead of 20 μA) and an increased U_{stop} (250 instead of 100 mV) was set. After adding a conducting salt and obtaining a conductivity of 9 mS/cm, the KF titration could be performed without problems with the standard parameters of the instrument.

3.4. Coulometry

The coulometric method is used for determination of small water contents. Here, iodine, required for the KF reaction, is produced at a generator electrode by anodic oxidation of iodide. The water content is calculated by measuring the intensity of current over the time.

The conductivity is of less importance for indicating the endpoint than for volumetric titrations, because of lower polarising currents at the platinum indicator electrode. On the other hand, the conductivity plays a key role in the generation of iodine. Therefore coulometric solutions must have a higher conductivity than volumetric solutions.

During water determinations and anodic oxidation of iodide, hydrogen is formed at the cathode. At the same time, the conductivity of the catholyte decreases because of diminishing ions. Therefore the capacity of the coulometric reagent is limited by the decreasing conductivity of the reagent.

Initial values of conductivity for common coulometric reagents are between 16 and 20 mS/cm. In cells with diaphragms, the capacity of the catholyte is reached at app. 4 mS/cm. During titration in one cell filling, the titration mode is adjusted to the decreasing conductivity of the catholyte by lowering currents at the generator electrode to a certain level.

In contrast to this, the current at the generator electrode, in cells without diaphragms, must stay at a high level (e.g. 400 mA), in order to guarantee a complete oxidation of iodide. Therefore coulometry without diaphragm is a little less robust for measuring conductivity than coulometry with diaphragm. Here, a limit value of app. 6 mS/cm is observed. Besides the limited titration capacity in standard reagents, consequences for analysing samples requiring the addition of dissolving media result. For example, a maximum amount of 20% toluene or long-chain alcohols can be added to Combicoulomat fritless (109257) in cells without diaphragm, in order to determine oils. In cells with diaphragms up to 40% can be added to the anodic compartment.

Therefore, developments of coulometric reagents aim to extend the lifetime of standard reagents and to increase the robustness after addition of less polar solvents for determination of special samples. This is reached by developing new compositions with a higher conductivity or compositions, characterised by a lower decrease of conductivity.

Scholz found that the addition of halogenated hydrocarbons to the catholyte has a positive effect on the capacity and on the lifetime of the reagent. While taking part in the cathodic reaction, CCl_4 is reduced with formation of $CHCl_3$ and Cl^- (Scholz, 1994). But since halogenated solvents are toxic, alternative substances have to be found.

With the addition of conducting salts, the initial conductivity of coulometric reagents can be increased. But when investigating reagents based on less polar solvents, such as ethanol or propanol, as alternatives for methanol, problems arise. Decreasing solubility and formation of agglomerates result in less successful attempts to increase conductivity. Furthermore, side reactions of the added substances and stability of the reagents have to be considered.

4. Conclusion

A minimum conductivity of the KF solution is one of the prerequisites for indicating the endpoint. By comparison of various one-and two-component systems, it was shown, that the lower limit depends on the type of the instrument and the settings of the titration parameters as well as on the solvent and its characteristic constant $E(I_2/I^-)$.

In methanolic standard solutions, optimum conditions for indicating the endpoint are ensured. Replacement of methanol by less polar alcohols, or titration with solvent mixtures with a low content of methanol, lead in many cases to non-reproducible overtitrations. Setting up new instrument parameters can reduce indication problems. Alternatively, the composition of KF reagents can be modified to reach a higher conductivity.

For one-component titration, the use of KF solvents with low concentrations of SO_2 and base, instead of pure solvents or solvent mixtures, is advantageous. Increased conductivity and, at the same time, increased reaction rate at the beginning of titration, lead to shorter duration of pretitration. Based on this knowledge, methanol-free solvents and KF solvents for the determination of oils and fats were developed.

In two-component systems, based on ethanol or propanol, the addition of conducting salts is favourable.

In coulometric reagents, additional problems occur with the replacement of methanol by less polar alcohols or solvent mixtures. Here the presence of supporting agents is absolutely essential, in order to ensure optimum conditions for the generation of iodine and for the indication of the endpoint.

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