The elpasolite method

Thermometric titration of sodium, aluminum and fluorine

In order to obtain a sharp endpoint and therefore reproducible results with potentiometric titration methods, the reactions upon which the titration is based must result in sufficiently large alterations in electrochemical quantities in the solution to be titrated. In thermometric titrations such alterations can be considerably smaller and still produce extremely accurate results – only one of the many advantages of this method! A typical example of a thermometric titration is the less well-known exothermic reaction (see Equation 1) in which the mineral elpasolite (NaK_2AlF_6) is formed from sodium, potassium, aluminum and fluoride ions. The industrial determinations of sodium, aluminum and fluoride are based on this reaction; these are all known as versions of the «elpasolite method».

$$Na^+ + 2K^+ + Al^{3+} + 6F^- \rightleftharpoons NaK_2AlF_6 \downarrow$$

Equation 1

Determination of sodium

Limitations of existing analytical methods

Sodium can be easily quantified in very small trace amounts by atomic emission spectroscopy (flame photometry, AES), atomic absorption spectrometry (AAS), inductively coupled plasma spectrometry in combination with atomic emission spectroscopy (ICP-AES) and ion chromatography (IC). However, these methods reach their limits if large amounts of sodium are present in the sample (g/L or percentage range). Samples that contain suspended solids can form deposits in the sample injection system (injector, nebulizer,..) or even block it completely. This means that one has to dilute highly concentrated solutions repeatedly in order to achieve the optimal working range of these analytical methods and instruments. The multiple dilution of solutions and the preparation of dilution series is not only very time-consuming, but also represents a possible source of error and easily leads to inaccuracies in the analytical results. In addition, the accuracy of AAS and ICP analytical methods is poorer than that of titration methods. In titrations the amount of analyte is directly proportional to the amount of consumed titrant. In contrast, in AAS and ICP the analyte concentration is proportional to the logarithm of the recorded signal.

Sodium in food that has been treated with sodium chloride can be quantified by a further method, in which the sodium content is estimated from the chloride content determined titrimetrically. The drawback of the method is obvious: sodium that is not present in the form of sodium chloride but originates from other compounds is not determined by this method. The sodium content determined in this way does not coincide with the real value, which means that it is possible that an incorrect value could be declared on the list of ingredients on the label.

Reliable and rapid determination of the sodium content with Titrotherm

With the 859 Titrotherm titrator, Metrohm offers an instrument for the direct determination of the sodium content by thermometric titration in numerous samples such as foodstuffs and sodium salts. This titrimetric method does not have the drawbacks and limitations mentioned above, but provides accurate results both quickly and reliably. The determination of the sodium content with the Titrotherm could not be easier: you only need to measure out the sample (e.g. grill sauce, see Fig. 1) into the titration vessel, add a conditioning solution and start the titration. The conditioning solution is a solution of ammonium hydrogen difluoride, which supplies the fluoride ions necessary for the reaction and adjusts the reaction solution to approx. pH 3. A solution containing 0.5 mol/L aluminum ions and 1.1 mol/L potassium ions is used as the titrant. The slight excess of potassium ions displaces the reaction equilibrium to the right (Equation 1) and the reaction proceeds to

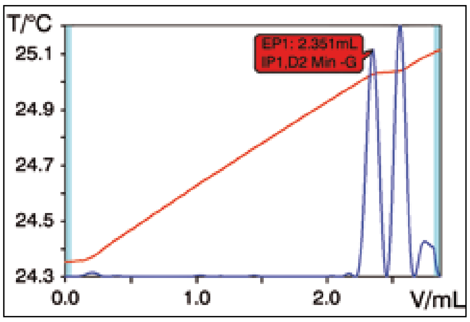

Fig. 1: Determination of the sodium content of a grill sauce.

The plot shows the titration curve in red (volume of titrant added vs. measured temperature of reaction solution) and the second derivative of this titration curve in blue. As the formation of elpasolite (Equation 1) is exothermic, the temperature increases until the endpoint is reached (endpoint marked; added titrant volume: 2.351 mL); this can be clearly recognized from the second derivative. After the complete formation of elpasolite the temperature initially remains constant, it then increases again due to the formation of K_3AlF_6.

completion. All the details of the sodium determination can be found in Metrohm Application Note H-061, which can be downloaded free of charge via an application search under **products.metrohm.com.** Table 1 shows the results of determinations of the sodium content of selected samples.

Table 1: Results of the determination of the sodium content of selected samples by thermometric titration based on Equation 1.

Sample	Sodium content (given as Na)
Tomato ketchup	908±4 mg/100g (n=7)
Sodium tripolyphosphate; technical grade	28.55±0.06% w/w (n=7)
Sodium lauryl ether sulfate (SLES); technical grade	4.10±0.04% w/w (n=7)

n = number of determinations

Determination of the aluminum content

The determination of the aluminum content is particularly important in the production of those aluminum-based chemicals that are primarily used for water treatment (e.g. flocculants) or in antiperspirant cosmetics. Two different methods for the determination of aluminum are widespread. The first method is based on the quantification of aluminum by back-titration. The sample solution containing aluminum is treated with an excess EDTA and briefly brought to boiling point to achieve complete complexing of aluminum with EDTA. After the solution has cooled down, the excess EDTA is back-titrated against a standard solution of zinc using visual endpoint detection. This analysis method is not only time-consuming, but demands a high degree of skill from the laboratory personnel.

The second method is based on the indirect determination of aluminum via quantification of the corresponding counterion. For aluminum chlorohydrate (antiperspirant) this method with the calculation of the aluminum content based on the chloride analysis produces an incorrect result. This is because the ratio Al:Cl varies depending to the production conditions[1].

In the case of sodium aluminate (intermediate product of bauxite digestion by the Bayer process) the second method can be used successfully for determining aluminum. This is a traditional method which is also used by aluminum refineries. The sodium content must be determined first before the aluminum content can be determined. As the sodium content is of no interest to many manufacturers, the direct and uncomplicated determination of the aluminum content by the elpasolite method is to be recommended. Sodium aluminate is used in water treatment, paper manufacture and in the production of synthetic zeolites.

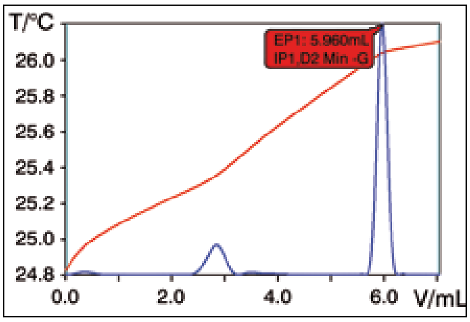

Fig. 2: Titration curve and its second derivative for the determination of the aluminum content of an aluminum chloride solution by thermometric titration.

In contrast to the classical titrimetric methods described above, the aluminum content of a sample can be determined rapidly and easily with a high degree of accuracy by thermometric titration. An example of such a sample is aluminum chlorohydrate, which is placed directly in the titration vessel. As aluminum must be present as Al^{3+}, the aluminum chlorohydrate is hydrolyzed by the addition of a small amount of concentrated hydrochloric acid. A special buffer is added to adjust the pH of the sample solution to a value of approx. 4.5 and also supply the necessary excess of sodium and potassium ions. This buffer solution is an acetate buffer that is made up of acetic acid, potassium acetate and sodium acetate. Sodium or potassium fluoride at a concentration of c = 1 mol/L is used as the titrant. More details about this method can be found in Application Note H-053, which can also be downloaded free of charge from **products.metrohm.com**.

[1] Empirical formula of aluminum chlorohydrate: $Al_2(OH)_xCl_{6-x}$ $0<x<6$

Sample	Aluminum content (given as Al_2O_3) *
Bayer aluminate solution (after precipitation of $Al(OH)_3)_2$) **	85.6±0.06 g/L (n=6)
Alum solution	4.76±0.0015 g/L (n=5)
Aluminum chloride solution **	10.39±0.006% w/w (n=11)
Aluminum chlorohydrate **	24.27±0.010% w/w (n=11)
Antiperspirant ***	8.38±0.003% w/w (n=7)

Tab. 2: Results of the determination of the aluminum content of selected samples by thermometric titration.

Remarks:

n = number of determinations
* : Generally valid industrial convention
** : Samples from customers
*** : Deodorant/antiperspirant containing aluminum chlorohydrate, from a supermarket.

Fluoride determination

Hydrofluoric acid (hydrogen fluoride, HF) and its salts are widespread constituents of acidic etching solutions such as are used in the manufacture of electronic components or in metal processing. Frequently, when a mixture of acids in aqueous solution is titrated against a base only a single endpoint is obtained. In such cases the separate determination of the fluoride content by titration with aluminum ions is the key to the quantification of all the components of the mixture. With the Thermoprobe, the temperature-sensitive sensor of the 859 Titrotherm, both acid-base and fluoride titrations can be monitored reliably. This makes thermometric titration a very versatile analytical method for solutions with a complicated composition that contain fluoride. Recently the Titrotherm has been successfully used for the analysis of a mixture of hydrofluoric acid, ammonium hydrogen difluoride and acetic acid. This required a fluoride titration with aluminum ions followed by a further titration with sodium hydroxide solution.

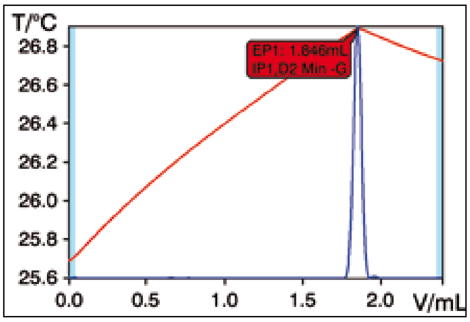

Fig. 3: Example of the determination of the fluoride content of a solution consisting of a mixture of hydrofluoric acid, ammonium hydrogen difluoride and acetic acid by thermometric titration.

Conclusion

With the aid of thermometric titration, the elpasolite method offers a quick, reliable and extremely accurate method for determining sodium, aluminum and fluoride ions in numerous different sample matrices. The 859 Titrotherm from Metrohm is the suitable favorably-priced instrument for these determinations.