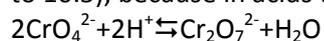


## 11. The argentometric determination of chlorides in food by the method of Mohr. Comparison of the Fajans, Mohr, and Volhard recipes

Argentometric methods belong to the group of volumetric precipitation ones. This means that during titration the almost insoluble product is formed, in argentometry this are silver(I) halogens<sup>1</sup>. The most popular are three methods from this group, named as their inventors: Mohr<sup>2</sup>, Volhard<sup>3</sup> i Fajans<sup>4</sup>. All these methods use AgNO<sub>3</sub> solution of known concentration, the Volhard one also solution of KSCN or NH<sub>4</sub>SCN.

In the **Mohr method** the content of chlorides is determined by means of titration with silver(I) nitrate(V) solution, the indicator is potassium chromate, K<sub>2</sub>CrO<sub>4</sub>. This method is also applicable for bromides. Anions which form insoluble salts with silver disturb this titration (PO<sub>4</sub><sup>3-</sup>, CO<sub>3</sub><sup>2-</sup>, AsO<sub>4</sub><sup>3-</sup>, etc.), as well as cations which precipitate as chromates (like Ba<sup>2+</sup> or Pb<sup>2+</sup>) or redactors which could reduce Ag<sup>+</sup> to metallic silver. When all chlorides react with silver, its excess reacts with chromate anions forming red-brown precipitate of Ag<sub>2</sub>CrO<sub>4</sub>. This method has limitations: its environment should be neutral or slightly alkaline (pH from 7 to 10.5), because in acids the chromates are converted to dichromates:



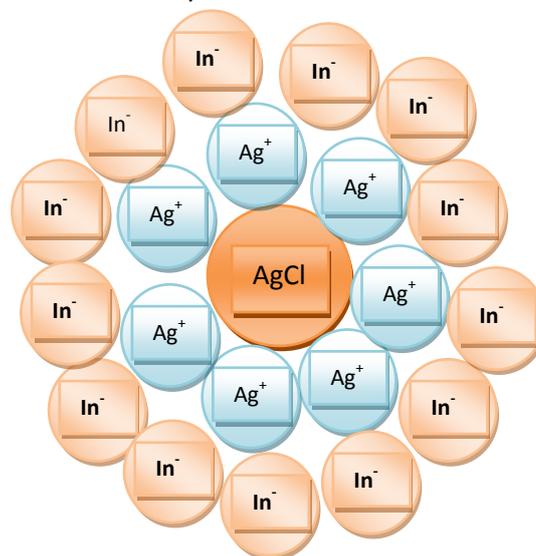
but silver dichromate is well soluble in water and the color of the chromate of Ag(I) will be not visible. On the other hand, in alkaline environment silver will precipitate as hydroxide, which in turn will convert to dark silver(I) oxide:



Moreover, in the Mohr procedure the amount of added indicator is important, because it affects the accuracy of analysis (compare solubilities of silver chloride with silver chromate). Finally, the neutral or slightly alkaline environment of reaction is its fault because transition metal ions eventually present in sample will disturb it if only they form color hydroxides.

**The Fajans method** of chloride determination employs an adsorption indicator. The indicator reaction takes place at the surface of the precipitate. The indicator is a weak acidic dye and exists in solution in the ionized form, In<sup>-</sup>. The titrant is a silver nitrate solution, and during the titration a precipitate of AgCl is formed. Initially this precipitate is colloidal, consisting of very small nonsettling particles with a diameter of less than 1 μm. While this would be undesirable for a gravimetric determination (colloids cannot be filtered), it is advantageous for an adsorption indicator method. What happens is the following:

Precipitates have a tendency to adsorb “their own” ions to the surface to form what is known as the primary adsorption layer, i.e., AgCl preferentially adsorbs Ag<sup>+</sup> or Cl<sup>-</sup>, whichever happens to be in excess. A colloidal precipitate has a very large surface area and, therefore, presents an abundance of room for adsorption. Before the equivalence point of the titration of Cl<sup>-</sup> with Ag<sup>+</sup>, the Cl<sup>-</sup> ion is in excess and forms the primary adsorption layer on the surface of



<sup>1</sup> Halogens – the common name of the fluorides, chlorides, bromides, iodides, by analogy also astatides and the salts formed by ununseptium – the synthetic element with atomic number 117, first observed in Dubna (Russia), in 2009.

<sup>2</sup> Karl Friedrich Mohr (1806-1879) – German pharmacists and chemist. Invented the Mohr salt, as well as the balance for determination of specific weight of a liquid (Mohr balance).

<sup>3</sup> Jacob Volhard (1834-1910) – German chemist. Together with his student Hugo Erdmann invented, among others, the Volhard-Erdmann cyclization reaction.

<sup>4</sup> Kazimierz Fajans (1887–1975) - an American physical chemist of Polish origin and a pioneer in the science of radioactivity.

the AgCl precipitate. The particles have a negative surface charge and repel each other; the colloid is stabilized by this. The indicator ion,  $\text{In}^-$ , is also repelled and stays well away from the surface.

Because the particles are negatively charged, they attract cations that are in solution more strongly than anions. Thus there is weakly bound secondary adsorption layer consisting of the cations.

Beyond the equivalence point,  $\text{Ag}^+$  is in excess and the surface of the precipitate becomes positively charged, with the primary layer being  $\text{Ag}^+$ . These positively charged colloidal particles will now attract the indicator anion and adsorb it into secondary adsorption layer.

The indicator forms a colored complex with silver ion, imparting a color to the precipitate. Only at the surface is the silver ion concentration high enough for the solubility product of the complex to be exceeded; this does not happen anywhere else in the solution, and the color is therefore confined to the precipitate surface.

The pH must be controlled for reliable results. If it is too low, the indicator (a weak acid) is dissociated too little to produce enough  $\text{In}^-$ . In the case of Fajans method, dichlorofluorescein<sup>5</sup> is the preferred indicator and it gives good results at pH values around 7.

Since the end point does not exactly coincide with the equivalence point, in more precise analyses the titrant should be standardized by the same titration as used for the sample (this eliminates the inherent error).

Photodecomposition of AgCl, creating a purple-black hue on top of the white AgCl, is another source of error. It should be minimized by carrying out the titration expeditiously and in relative low light. As explained above, a colloidal precipitate is preferred in this titration. At the equivalence point, neither titrant nor titrate ions are in excess, and the precipitate is momentarily without a surface charge. This causes the colloidal particles to coagulate, thereby reducing the precipitate surface area. It can be prevented by the addition of a small amount of dextrin (hydrolyzed starch) to the solution.

The titration reaction is as follows:  $\text{AgNO}_3 (aq) + \text{NaCl} (aq) \rightarrow \text{AgCl} (s) + \text{NaNO}_3 (aq)$

In fact, because neither the  $\text{Na}^+$  nor  $\text{NO}_3^-$  ions are involved in the reaction, this reaction may be written more accurately as:  $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}(s)$

The nitrate ions are only weakly adsorbed to the precipitate after the equivalence point is reached, and they are easily displaced by indicator ion. The end point is signaled by the appearance of the pink color of silver dichlorofluoresceinate.

As opposed to the above two procedures, the **method of Volhard** is a reverse titration. All halogens and also thiocyanates can be analyzed using it. One adds to the sample a known amount of silver(I) nitrate, in excess. The sample is acidified using nitric acid,  $\text{HNO}_3$ , and the excess of silver is determined by titration with potassium or – preferably – ammonium thiocyanate. The indicator is iron-ammonium alum (sulphate). When all the silver will be precipitated by thiocyanates, their excess form red complex with  $\text{Fe}^{3+}$  ions, of the general formula  $\text{Fe}(\text{SCN})_n^{3-n}$  ( $n = 1$  to  $6$ ) signaling the end-point of titration.

When chlorides are analyzed, the Volhard method has to be slightly modified. During titration, the solution is in contact with two precipitates simultaneously: AgCl and AgSCN, which have different solubility (AgSCN is less soluble than AgCl). So, after titration, the excess  $\text{SCN}^-$  ions react with the AgCl in precipitate, and the red color of the iron-thiocyanate complex gradually disappears; this takes seconds to one minute. Addition of next portion of  $\text{SCN}^-$  restores it, but after short time the process repeats. This could lead to huge error in analysis. In other words, the thiocyanate ions displace the chloride ones in the precipitate at the expense of the indicator complex. To avoid this, the simple idea is to separate the precipitated AgCl from the solution by filtering and titration of the filtrated solution, but there exists much simpler idea. Before titration with thiocyanates, one adds to the solution few cm<sup>3</sup> of an organic liquid which does not mix with water (chloroform, nitrobenzene etc.). This compound will moisten the surface of

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<sup>5</sup> Dichlorofluorescein indicator is typically 0.2 g in 100 mL of 3:1 ethanol:water. Eosin tetrabromofluorescein is suitable for titrating against bromide, iodide, and thiocyanate anions, giving a sharper end-point than dichlorofluorescein. It is not suitable for titrating against chloride anions because it binds to AgCl more strongly than chloride does.

the precipitate forming on it a film (layer) insoluble in water and thus isolating it from the solution. This effectively prevents any exchange of ions between precipitate and solution.

The Volhard method is more precise than the former ones, but its main advantage is acidic environment of reaction. Its faults are time-consumption (more operations) and higher costs, in particular higher consumption of silver nitrate.

In this task the students will make two experiments:

- I. Analysis of salt in a food sample (chips, sausage etc.) – here limited to the Mohr method.
- II. Comparison of the three methods mentioned above, the aim of this is comparison of their preciseness, easiness of observation of the end-point, etc. Note that the sample which the students will analyze is neutral and no operations for correcting its pH are necessary.

## Experiment no. 1

### Procedure

#### **A (Analysis of chips, sausage, cheese etc.):**

- Weigh ca. 1 g of the food using the analytical balance.
- Grind the cheese (or sausage or chips) into very small pieces.
- Add ca. 50 mL of hot water and shake during 2-3 min.
- Filter the solution, washing the remaining solid sample with few small portions of hot water.
- Wait until the filtrate cools down.

#### **B (The sample is butter):**

- Weigh ca. 2 or 5 g of the butter (depending on the butter is salted or not) using the analytical balance.
- Add ca. 100 mL of boiling water and mix 5-10 min until homogeneous emulsion is formed. Check pH – if it is below 6.5, add  $\approx 0.1$  g of solid  $\text{CaCO}_3$ .
- Wait until the mixture cools down.

#### **Further procedure is identical for A and B:**

- Add ca. 2 mL of indicator ( $(\text{NH}_4)_2\text{CrO}_4$ ) and few drops of dextrin solution.
- Titrate the solution in diffuse light with constant swirling, using  $0.05 \text{ mol}\cdot\text{L}^{-1}$  silver nitrate solution (present in the main lab, in automatic burettes – ask the teacher how to operate it). The silver chloride flocculates shortly before the equivalence point is reached. At the equivalence point the precipitate suddenly turns brown.
- For each titration, calculate the weight percent chloride in the sample (to two decimal places).

### Report

- Make at least two (better three) independent analyses.
- The mean of these two (or three) determinations as your final answer. Also report the relative standard deviation (as a percentage) of the determinations.

## Experiment no. 2

### Procedure (The sample is pure NaCl in solution, it is dispensed in the volume flask a 250 mL):

- Add water to the mark, mix the content of the flask carefully.

#### **A Mohr Method**

- Take 1 pipette of the solution to the Erlenmeyer flask, add water to ca. 150 mL and ca. 2 mL of indicator ((NH<sub>4</sub>)<sub>2</sub>CrO<sub>4</sub>).
- Titrate with constant swirling, using 0.05 mol·L<sup>-1</sup> silver nitrate solution (present in the main lab, in automatic burettes – ask the teacher how to operate it). The silver chloride flocculates shortly before the equivalence point is reached. At the equivalence point the precipitate suddenly turns brown.
- Repeat titration, if necessary even three times.

#### **B Fajans Method**

- Take 1 pipette of the solution to the Erlenmeyer flask, add water to ca. 150 mL, few drops of dextrin solution and few drops of indicator (dichlorofluorescein)
- Titrate with constant swirling, using 0.05 mol·L<sup>-1</sup> silver nitrate solution. At the equivalence point the precipitate suddenly turns pink.
- Repeat titration, if necessary even three times.

#### **C Volhard Method**

- Take 1 pipette of the solution to the Erlenmeyer flask, add 5 mL of HNO<sub>3</sub> (1+1 – it is in the fume hood) and add water to ca. 100 mL.
- Add from burette exactly 50 mL 0.05 mol·L<sup>-1</sup> AgNO<sub>3</sub> solution.
- Add 3 mL of nitrobenzene (in fume hood) and 1 mL 10% iron-ammonium alum acidified with nitric acid; shake the flask during 1 min.
- Titrate the excess of silver added using 0.05 mol·L<sup>-1</sup> KSCN. The end-point is visible as red-brown color.
- Repeat titration, if necessary even three times.
- For each titration, calculate the weight percent chloride in the sample (to two decimal places).

### Report

- Calculate the arithmetic means for each analysis independently. Calculate also their standard deviations (as the % of the mean).
- Compare the obtained results and comment the differences between them, as well as the differences between their preciseness.

### **Waste Disposal**

Deposit all precipitates and silver waste solutions in the appropriately marked containers.

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#### Sources:

[http://chemistry-teaching-resources.com/Investigation\\_Ideas\\_files/Chloride%20by%20Fajans%20Method.pdf](http://chemistry-teaching-resources.com/Investigation_Ideas_files/Chloride%20by%20Fajans%20Method.pdf)

Wikipedia

textbooks