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A luxury item with analytical demands

Titration of salt content in caviar

Where caviar used to be a luxury article for the more privileged level of society, today, modern sturgeon farms allow access for the wider masses. However, for caviar to fulfill the high expectations of the consumers, the goods must be inspected regularly. In order to quickly respond to deviations, the analysis meters must offer high precision and reliability.

Caviar is the name for roe (eggs) collected during fishing, while only the roe of certain sturgeons is considered "real caviar". Table 1 shows a summary of these types of sturgeons as well as general characteristics of real caviar [1].

Sturgeon	Hausen (Huso Huso)	Waxdick (Acipenser gueldenstaedti)	Sternhausen (Acipenser stellatus)
Type of caviar	Beluga	Osietra	Sevruga
Grain size	1 - 2 mm	around 1 mm	< 1 mm
Appearance	Grey/brown to black		
Structure	tender skin, not tough, grainy, soft, smooth		
Odor, taste	Immanently comfortable		

Table 1: Evaluation criteria of real caviar as per [1]. The grain size are usually larger, while grain sizes > 3 mm are typical for Beluga, approx. 2 mm for Osietra and max. 1 mm are typical for Sevruga [2].

However, other sturgeon and fish types are used to harvest caviar as well. Examples of these include salmon caviar, trout caviar and caviar from the lump fish * so-called "German Caviar"). The eggs consist mostly of proteins, fats, minerals and vitamins. The energy content of 100 g of caviar is approx. 1,100 kJ, the water content is 53 to 58 % [2] depending on the type of caviar. The eggs contain all important nutrients needed to feed the fish's offspring.

A different economic value is attributed to the different types of sturgeons, especially when farm raised. While Husa Husa needs 14 - 20 years to sexual maturity [2], Osietra and Sevruga can be harvested significantly earlier. This is also one of the reasons why Beluga caviar is among the most expensive of the types of caviar available. Even more expensive is the so-called white caviar, which is harvested from sturgeons suffering from pigmentation disease (albinos) and which features a yellow/white color. This caviar is considered the most expensive food in the world, as only approx. 8 kg are harvested per year [3].

Based on the large demand of earlier years, the number of sturgeons in the wild has decreased rapidly [2]. All types of sturgeons are almost extinct today and have been under protection by the Washington Convention (CITES) since April 1, 1998. As a consequence, the prices for caviar have increased drastically. Modern sturgeon farms contribute to the conservation of the sturgeons today. The experiences gained in the past few years and the associated progress in the raising of these sturgeons has caused the quality of the caviar to improve and the prices to decrease. Therefore, you are able to find reasonable caviar types for sale today. Nevertheless, caviar is and will be a luxury treat for special occasions.

As caviar spoils quickly, the harvesting requires speed and cleanliness. The roe is located in the ovaries of the female sturgeon. The removal of the eggs should take place prior to them reaching their maximum maturity. Also, the color of the eggs depends on the degree of maturity. Once the correct time is reached, the females are slaughtered and cleaned immediately. The cleaning process is very important as constant bacteria can contaminate the roe. Afterwards, the ovaries are removed with the eggs and pressed through a strainer with a mesh grid of approx. 4 to 6 mm. This releases the eggs from the

adhesive skins of the ovaries. The harvested eggs are mixed with salt and filled into cans, which are sealed airtight. This entire process must take place quickly as the eggs will quickly spoil when exposed to air [2].

Adding salt is usually the only method to preserve the caviar. In some countries, boric acid is added as well. In the US and Europe, boric acid is prohibited, but about 4 g / 100 g of product is allowed as an additive for caviar imported into Europe. We assume that the side effects of the boric acid ingested with the usually small amount of caviar do not bear any importance. Caviar is usually stored at 0 to -2 °C [2]. There are usually three reasons why caviar spoils: fermenting degradation by enzymes in the tissue, fat oxidation as well as bacterial growth [2].

The salt used as a preservative can vary in its concentration and processing. Caviar with a salt content of 2.8 to 3.5 % is called Malossol (mildly salted). With a caviar of lower quality, 7 - 10 % salt are added (heavily salted). With so-called pressed caviar, the cleaned eggs are salted wet in a saturated salt solution. This process takes place at 40 - 45 °C. After about 2 - 3 minutes in the salt brine, the roe is removed by means of sieves and the remaining salt brine is pressed through linen cloths. This process is used for caviar of lesser quality or mixtures made of different types of caviar [2].

A regular inspection of the salt content in the finished product is necessary to be able to offer the customer consistent quality. Deviations from the nominal values cause loss of quality or larger quantities of raw materials being used. The consequences are economic losses, complaints and customer dissatisfaction.

The inspection of the salt concentration is performed by means of titration of the chloride content. Figure 1 and 2 show the set up by means of a TitroLine® 7000 with electrode and homogenizer. The homogenizer is used to cut the weighed sample into smaller pieces



Figure 1: TitroLine® 7000 set-up

and thus achieve a more even distribution. Even only 0.5 to 1 g of sample are sufficient to determine the content. The titration solution used is a 0.1 molar silver nitrate solution. During the titration, the silver ions of the titrator react with the chloride ions present in the sample of the added salt and form a poorly soluble silver chloride precipitation. The detection is made by means of silver electrode coated with an AgCl layer (AgCl 62). Based on its silver chloride coating, this electrode is especially suitable for the detection of the poorly soluble AgCl created during the titration process. As an inner electrolyte, a 2 molar KNO₃ solution is used, which is saturated with 0.001 mol/l KCl. This minimizes a contamination of the sample solution with chloride ions. The pH value of the sample solution is adjusted with nitric acid. An acidification is necessary, as otherwise, silver hydroxides could interfere with the reaction.



Figure 2: Homogenizing the sample

The TitroLine® 7000 is supplied with various standard methods that also include the determination of the chloride concentration. The titration takes place dynamically and is terminated at the equivalence point. Figure 3 shows the standard parameters of this determination. Figure 4 shows a sample curve for a chloride titration and their first derivation as a termination criterion. The output of the result as NaCl takes place after by simple adaptation of the factor used in the calculation.

Methodenname:	NaCl in %	Erstellt am:	11.02.16 09:46:41
Methodentyp:	Automatische Titration	Letzte Änderung:	11.02.16 09:48:20
Messwert:	mV	Dämpfungseinstellung:	Keine
Titrimationsmodus:	Dynamisch	Dokumentation:	GLP
Dynamik:	Steil		
Messgeschwindigkeit / Drift:	Benutzerdefiniert:	min. Wartezeit:	03 s
		max. Wartezeit:	15 s
		Messzeit:	03 s
		Drift:	10 mV/min
Startwartezeit:	0 s	Rührersteuerung:	frei
Titrimationsrichtung:	Steigend		
Vortitration:	Aus		
Endwert:	Aus		
EQ:	An (1)		
Steigungswert:	Benutzerdefiniert	Wert:	400

Figure 3: Standard settings of a chloride titration

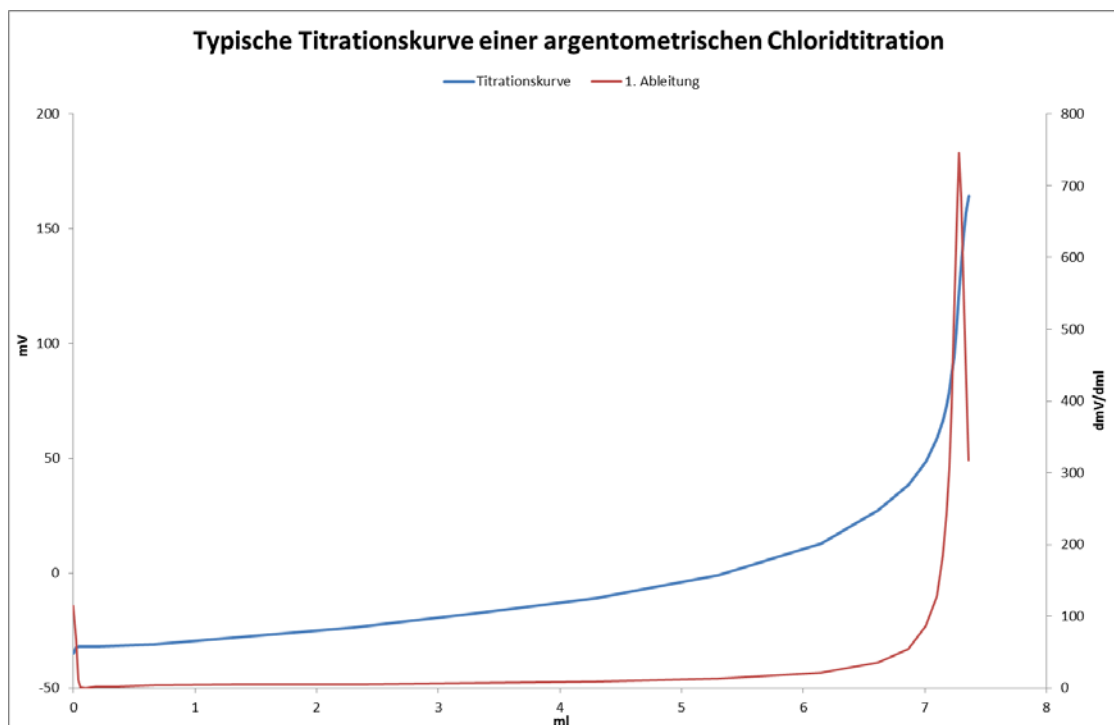


Figure 4: Typical titration curve of an argentometric chloride titration

Conclusion

Caviar has reached wider masses thanks to modern sturgeon farms, but still remains a luxury product in spite of sinking prices. The consumer has certain expectations for this luxury product that the manufacturer must meet. The salt content of the finished product bears a large importance here. This must be in the correct range to ensure a sufficient

preservation and to fulfill the taste expectations of the customer. A regular inspection of the salt content is very important as this is the only way to quickly respond to deviations and to prevent economic damage. The titration offers a simple and reliable method to control this important parameter.

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Literature:

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