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ANALYSIS OF SODIUM AND POTASSIUM IN MEAT PRODUCTS

D. KÜHNE

Federal Centre for Meat Research, Institute for Technology, D-8650 Kulmbach, Federal Republic of Germany

SUMMARY

In this paper the measurement of sodium and potassium concentration in meat products is described with ion-sensitive electrodes and flame-photometry. We show the advantages and limitations of measurement with ion-sensitive electrode and explain the mathematical formula used for the correction of measured values when there occurs a drifting with time and nonlinear calibration curves. Concentrations of sodium and potassium are comparable with both methods and with the results of determination of common salt via chloride. The two methods can be recommended for the exact determination of both elements.

INTRODUCTION

The consumption of common salt (sodium-chloride = NaCl) with the food is so high in industrial countries that there exists a latent health risk. For predestined people a connection between high blood-pressure and intake of sodium has been proved. Diets with a reduced salt-content and low salt meat products are recommended and developed in many places. Potassium as antagonist of sodium is regarded as an element with favorable physiological effects and salts of potassium can replace common salt preferably. Therefore the exact estimation of sodium (Na) and potassium (K) in meat and meat products if of special interest.

The present official method for the estimation of common salt is based on the estimation of chloride. So the more important physiological effect of Na from common salt will not be considered and incorrect results may arise from application of other chlorides. Therefore and in special consideration of small laboratories we examined two convenient methods with low costs and high reliability. The methods of estimation of Na are the same as for K, so we tested also the methods for K.

For estimation of Na the following methods can be used

1. Gravimetric with Uranylacetat
2. Flame-Photometry (Emission - AES, or Absorption - AAS)
3. Potentiometric with ion-sensitive electrode
4. Neutron Activation
5. Nuclear Magnetic Resonance
6. Plasma Spectrometry

As a gravimetric method #1 will not be a fast one, furthermore working with the heavy metal uran cannot be recommended. Method #4, #5 and #6 are very costly and can be used only in special laboratories. For the estimation in normal and small labs methods #2 and #3 remain. These methods are described here, the results are compared with each other and with the results obtained by the determination of chloride.

IONSENSITIVE ELECTRODE

Between the electrochemical potential U, measured with a Na-sensitive electrode and the activity a of Na-ions exists the relationship is described by the equation :

$$U = Uo' + S * \lg a/ao$$

If the coefficients of activity are the same in the solution of sample and standard, e.g. in a buffered solution, the equation can be simplified :

$$U = Uo + S * \lg c/co \qquad (1)$$

The buffered standard solutions used had a concentration of 0.01, 0.1 and 1 g NaCl/l in a 1/8 m buffer (made from 37.3 g Triethanolamin = 1/4 Mol and 10.35 ml conc.HCl = 1/8 Mol).

In equation (1) Uo represents the basic potential, S is the Nernst factor and c the concentration of Na. For direct estimation a calibration curve for estimation of Uo and S is needed. As control the value of S should be near the theoretical value, with $S = R * T * \ln 10 / F$; T means the temperature in degrees Kelvin, R, F and ln10 are constants. The value of S is 58.17 mV for 20 degree and 59.16 mV for 25 degree Celsius. The lower the value measured the worse the electrode has to be judged. As a limit for the acceptable value of S for the sodium-electrode 56 +/- 2 mV is recommended. We measured this value as the difference of the potential of two buffered solutions, one with the 10-fold concentration of the other. Transposition of equation (1) results in :

$$C = Co * 10^{(U-Uo)/S} \qquad (1a).$$

The results from this measurement showed that the basic potential Uo was not very constant. So we judged the method as not very accurate and didn't use it.

In the next step we tested the method with addition of sample solution to buffered standard solution (Analat-method) and the other way of addition of standard to sample solution. For practical reasons we decided later to use the first way of addition. The resulting concentration has to be calculated from both solutions with the formula :

$$C = (Cx * Vx + Cs * Vs) / (Vx + Vs) \qquad (2)$$

with C = resulting concentration
Cx= concentration of the sample solution
Vx= volume of the sample solution
Cs= concentration of the standard solution
Vs= volume of the standard solution

Substitution of (Vx + Vs) / Vs by k results in :

$$C = 1/k\ (Cs + Cx * Vx / Vs) \qquad (2a)$$

With this substitution equation (1) can be written :
$Ud = S * \lg C/Cs = S * \lg (1/k * (1 + Cx*Vx/Cs*Vs))$
with Ud as difference of voltage of solutions with concentration C and Cx. The equation for Cx is :

$$Cx = \frac{Cs * Vs}{Vx} * (k * 10^{Ud/S} - 1) \qquad (3)$$

For measurement of several samples the values of Cs, Vs, Vx und S remain the same and can be combined as a constant for calculation. The only variable for estimation of Cx is Ud. The method described has proved to be the best and was used later exclusively. The calculation-modus is integrated in some measuring instruments for ionsensitive electrodes but it can be realized with a programable pocket-calculator, too.

A third method has been tested especially for theoretical reasons. Here a standard is added twice or more to the sample solution. The evaluation is known as "Gran's-Plot" (GRAN, Analyst 77, 661, 1952). With this method only the volume and concentration of the added standard solution has to be known for calculation of the unknown sample concentration. The first step when applying this method is the calculation of S by an iterative approximation with the formula :

$$S = Ub / \lg \frac{2 * k * 10^{Ua/S} - 1}{2 * k - 1} \qquad (4)$$

with Ua as difference of voltage after first addition and Ub after first and second addition. The calculated values of S showed great changes for small differences in Ua or Ub and partially S differed significantly from the theoretical value. Besides this methodical problem the method was very time consuming. Therefore we didn't use it in practice.

For practical measurement of Na we added 5 ml of extracts of meat products for estimation of nitrite, nitrate and chloride (10 g of sample, diluted to 200

ml) to the suitable standard solution and measured the differnce in voltage. The values were in very good agreement with those from chloride-determination (correlation coefficient = 0.9973). Because of the time-consuming preparation of the sample solutions and the need of laboratory equipment we tested additionally a faster method which can be applied outside a laboratory.

FAST ESTIMATION OF SODIUM

About 200 mg of a homogenized sample is given to a standard solution. This sample contains the same amount of Na as the 5 ml solution mentioned earlier. The homogenized sample should have a great surface for faster diffusion of Na. The exact weight is determined by difference weighing. From this amount and the difference in voltage before and after addition to the standard solution the concentration of Na is calculated. The results showed a lower correlation coefficient and a higher scattering related to the chloride-values. The main reason for this result is seen in the small and not representative amount of the sample. So one has to decide for fast and less exact or slower but more accurate results.

FLAME-PHOTOMETRY

In laboratories for medical purpose Na is determined mainly by flame-photometry. We used a spectrophotometer for atomic absorbance or flame emission measurement with digital reading, burner with air and acetylene, working in emission-mode. As first we found that the range of measurement is remarkable smaller than with ion-sensitive electrodes. With higher concentrations the calibration curve is distinctly nonlinear and for smaller concentrationes the scattering of the signal becomes to high, related to the mean value of several measurements. Secondly there was a drift of the signals with time. This effect can be recognized mathematically by the following formula :

$$C = \frac{cx - bo - x\,(b1 - bo)}{ao - bo - x\,(ao - bo - a1 + b1)} * V \qquad (5)$$

The symbols mean :

a = signal for the highest standard concentration
b = signal for aqua dest. (concentration = 0)
ao,bo = signals for a and b before the beginning and
a1,b1 = signals for a and b after the end of measurement of sample solutions
cx = signal of a sample solution at the time x
x = value between 0 (begin) and 1 (end), characterizing the time of measurement
V = product of all factors of dilution with the highest standard concentration
C = concentration in the sample

Because of nonlinear calibration curve we tried to characterize the function. The curve flattened more and more with higher concentrations and was in best accordance (measured by correlation coefficient) with a function of the form :

$$y = s * x^{r} \qquad (6)$$

For the calculation of the values of s and r before the sample solutions and between a and b the so-called halfconcentration, containing half the concentration of the highest standard, was measured additionally. Other functions which can be linearized, can be applied by this scheme, too. We gave the digital signal of the photometer direct to a programable calculator (HP 97). Following a certain cycle after the measurement of all standard and sample solutions the results were calculated automatically. The cycle was as following :

1. solutions of zero-, half- and highest standard
2. solutions of samples (max. 12)
3. solutions of zero- and highest standard

Within one cycle at first mean values and standard deviations of several measurements of all solutions were printed. After printing out the value of the last solution drift and nonlinear correction of the values followed automatically. The principle of this corrections can also be used for other analytical methods. The results of measurements were compared with the results for the same samples from ion-sensitive electrode. Concentrations of common salt in meat products are in the region of 1 to 4 %. The correlation coefficient for this comparison was higher than 0.99, so we recognize both methods as good to use.

ESTIMATION OF POTASSIUM

For the estimation of potassium the same methods as for Na can be applied. We realized measurements with ion-sensitive electrodes from one solution with three electrodes one for Na and one for K and a reference-electrode. The number of analysis carried out so far are not as large for K as for Na but the values for the measurement with ion-sensitive electrode and flame-photometer fit as well as those for Na. Therefore we suppose that both methods are qualified for estimation of Na and K.

MEASUREMENT WITH A CURE TESTER

For the estimation of common salt we tested the suitibility of a cure tester who measures the electrical conductivity with an alternating current of high frequency. The cure tester is recommended for judging the degree of curing. We observed that the size of the dielectricum influenced the signal. This indicates that different results will be obtained for intact and destroyed muscle cells. Raw sausage (salami-type) showed smaller scale-numbers with the time of storage and the lower water content connected with it. To the centre of the sausage the concentrations of water and salt increase and higher scale numbers confirm this fact. Additionally other ions as free amino or fatty acids and metabolites as lactate influence the conductivity. Because of the many influences measurements with the cure meter cannot replace the ion-specific estimation of Na or K. This will not exclude that trained experts can judge with this instrument the state of curing in an defined product like ham.