Observation on the measurement of the reduction and oxidation potential of processed meat products

WALDEMAR UCHMANN and JOZEF GRACZ
Institute of Food Technology of Animal Origin, Agricultural University of Poznań, Poland

One of several important factors influencing the course of processes in biological systems is their reduction and oxidation ("redox" potential). Its character is also a good indicator of occurring processes. However, in spite of its advantages, this indicator is relatively rarely used in investigations because of methodical difficulties.

Electrometric methods are the most reliable measuring methods of the redox potential.

In conformity with an accurate definition the redox potential is the potential of an electrode of non-active material (e. g. platinum) immersed in a solution maintaining a reduction and oxidation balance. This potential is measured in millivolts against a normal hydrogen electrode. In such a measuring system the redox potential (E) is expressed by the equation:

$$E_h = E_0 + \frac{RT}{nF} \lg \frac{[ox]}{[red]} + \frac{n-a}{n} \cdot \frac{RT}{F} \ln [H^+] \qquad (1)$$

where: E_0 – normal redox potential
a – number of hydrogen ions formed in a reduction reaction
n – number of hydrogen atoms necessary for the reduction
R – gas constant
F – Faraday's constant
$[ox]$ – concentration of the substance of oxidized form
$[red]$ – concentration of the substance of reduced form

If $\frac{[ox]}{[red]} = 1$ then the other part of the equation (1) = 0. If at the same time pH = 0 then $E_h = E_0$.

For pH values other than zero, but precisely defined, the expression:

$$E_0 + \frac{n-a}{n \cdot F} \cdot \frac{R \cdot T}{n \cdot F} \cdot \ln [H^+] \quad \text{has a constant value.}$$

This is why on expressing measured results in mV, as a measured value of E_h, the occuracy is low since the obtained values depend upon the concentration of hydrogen ions in the examined medium. In case of any deviation from this concentration deviating results are obtained.

Therefore, two additional terms were introduced:

– "redox" exponent

$$pE = \frac{2F}{R \cdot T} \cdot E_h \tag{2}$$

– value rH:

$$rH = -\lg (H_2) . \tag{3}$$

The value rH defines oxidation and reduction intensity of the system. Using the above terms we may convert equation (1) into:

$$E_h = \frac{RT}{2 \cdot F} \cdot rH - \frac{RT}{F} \cdot pH \tag{4}$$

or:

$$rH = \frac{2 \cdot F}{R \cdot T} \cdot E_h + 2pH . \tag{5}$$

To measure the "redox" potential in a medium of 20°C (293°K), the above formula takes the form:

$$rH = 0{,}0343 \cdot E_h + 2pH . \tag{6}$$

The value pH calculated on the basis of equation (6) is the most objective form of presenting the findings of "redox" systems.

To establish this value, we measure the values $E_n \cdot pH$ of the system. In conformity with the definition the "redox" potential may be measured by means of a platinum or gold electrode together with a normal hydrogen electrode as reference electrode. In practice, a saturated calomel electrode (NEK) can replace the hydrogen electrode. But then take into account the difference of their potentials, which e. g. in temperature of 20 °C amounts to 249 mV and this may be expressed by the equation:

$$E_h = E + 249 \text{ mV} \tag{7}$$

where

E = difference of potentials of NEK – Pt.

The value pH is determined by a system of electrodes: NEK and glass electrode (ESz).

There is a possibility of evaluating rH by means of only two types of electrodes: platinum and glass electrodes.

Then:

$$rH = \frac{Ept - E_{szk}}{29.06} + C \ (20 \text{ °C})$$

where C is a constant dependent on the used glass electrode; pt = platinum and szk = glass. The constant can be established by means of rH buffers beacuse for instance the value rH of a satured solution of quinhydrone in a 0.1 *N* solution of HCl is 24.2.

The use of 3 types of electrodes gives anyhow more information about the examined system (E-, pH and rH). However, in such a case, a methodical difficulty arises because both the differences of potentials PT – NEK and those of NEK – E_{szk} should be determined at the same time for the same sample. During the preparation of samples avoid any operations influencing the "redox" processes taking place in a sample. All sorts of homogenization operations, i. e. processes which cause aeration of a sample and activation of enzymatic and microbiologic processes are particularly detrimental.

The best solution would be the measurements by means of electrodes immersed directly in the tested sample. A method of this type (for the measurement of E_h only) was described by F. Wirth and L. Leistner (1).

In order to determine the "redox" potential of a canned meat charge, they placed NEK and two platinum electrodes in it, and measured the difference of potentials between NEK and each of the Pt electrodes. The average of these two measurements was the result desired. These authors established the lack of statistically essential differences between these readings during a simultaneous existence of differences between the tested samples.

It verifies the existence of a considerable influence of the medium and the necessity of testing a larger number of samples in order to obtain representative results.

Our investigations

As a consequence of our preliminary investigations we have found that better results are obtained with the use of the system: one platinum electrode and two NEK electrodes.

However, the best solution is to place three electrodes: NEK, Pt and ESz directly in a sample and make at the same time a few repetitions. Successive connections of these electrodes offer the following combinations:

a) Pt – NEK

b) NEK – ESz

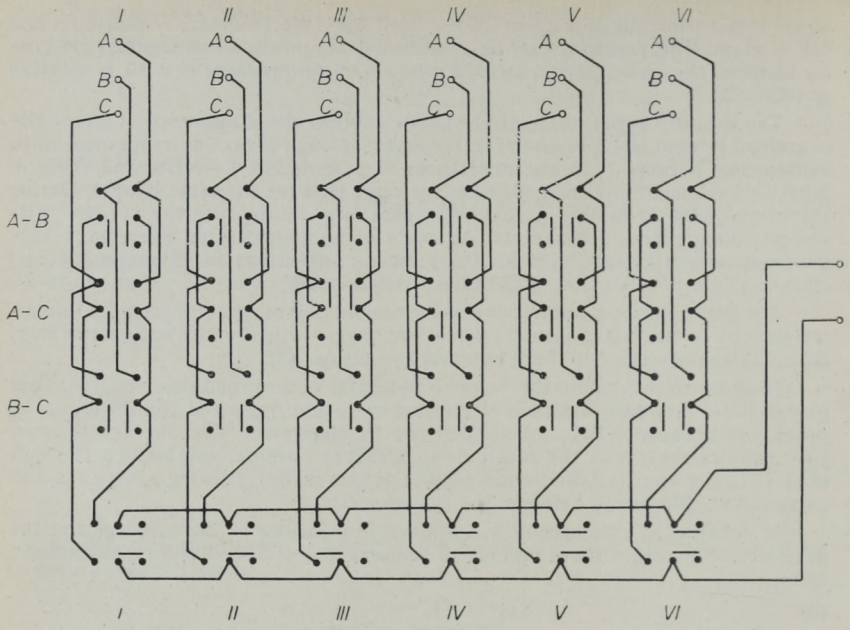
c) Pt – ESz

On the basis of readings of the combination "a" the value En may be calculated while from the combination "b" the value pH is obtained.

Through the transformation of these results we obtain the value rH (formula 5). Reading the combination "c" enables to calculate the value rH by means of the formula 8. In this manner the value rH may be determined in one sample by two different ways at the same time. By simultaneous measurements in a few samples a reproducible and representative result is obtained.

To facilitate successive connections of various electrodes to a meter, a special switch (diagram No. 1) was made our laboratory. Ends of individual electrodes are connected in this switch to plugs A, B and C.

Engagement of corresponding key – switches enables to connect to a meter the proper set of electrodes from a sample selected arbitrarily.



Scheme of the special switch

Care must be taken to a careful shielding of cables and to the earthing of the entire measuring system.

Owing to this switch the measurements of "redox" potentials can be made in many samples by means of only one meter and thus eliminating errors resulting from the diversification of accuracy of individual meters.

Table1

Results of determining the „redox" potential of some sausage farces

No	Farce	Result of determination							Standard deviation S (x)	Standard error S (x)	Confidence interval $\alpha = 0,05$	Variability ratio Vx
		1	2	3	4	5	6	average				
1	A	18,2	18,6	18,8	19,1	18,4	18,2	18,55	0,36	0,15	0,49	1,92
2	B	19,7	19,1	18,5	18,9	19,4	19,5	19,18	0,44	0,18	0,60	2,29
3	C	18,6	18,4	19,3	19,5	18,1	18,8	18,78	0,54	0,22	0,73	2,85
4	D	17,7	18,6	19,1	18,2	18,5	18,0	18,35	0,49	0,20	0,68	2,69
5	E	19,8	19,1	18,4	18,6	19,6	19,6	19,18	0,58	0,24	0,80	3,03

The elaborated method was applied to the measurement of the "redox" potential of cured pork stuffing and some sorts of processed meat.

On the basis of a number of tests the following procedure was established:

Samples of stuffing to be examined were put in glass test-tubes (dia. = 35 mm, h = 60 mm) placed in a wooden stand. It is advisable to locate this set in a larger vessel filled with inert gas (N_2). Electrodes were immersed in samples of the stuffing (NEK, usually by means of an electrolytic key). Electrode ends were connected to corresponding clamps of a switch coupled to a meter (pH-meter LBS – 66).

The construction of the described switch allows for a parallel investigation of six samples. Next, after a strictly defined time (e. g. 15 or 30 minutes), a switch was engaged to fix a sample in which tests were made (I – VI) and then within this sample, switches selecting a right combination of electrodes (A – B, A – C, B – C). All results read have to be recorded.

In this way the values of potentials were measured successively in all samples.

With the use of the obtained results and formulas (6 and 7), the values En, pH and rH were calculated.

Due to the wear of electrodes and to the possibility of damaging them, they have to be checked and calibrated each time before starting the tests. This was done by the measurement of the hydrogen ion concentration and "redox" potential of any "redox" buffer soluion. Only the lectrodes showing no deviation from the standard van be used for further investigations.

By means of the described method many measurements of the "redox" potential were made in various samples of a cured pork stuffing. A particular advantage of the presented method is the possibility of making cyclic tests i. e. those which require to make measurements in the same samples at various times, and characterizing the dynamics of changes of the "redox" potential of tested samples.

Some of obtained results are shown in Table 1. They were subjected to a basic statistical analysis. This showed that the developed method is of a high accuracy (V – 3%).

Owing to the described switch a large number of measurements (because of the short time for a single measurement: 10 – 15 secs) can be made at the same time. The switch allows to carry out measurements in a laboratory equipped with only one meter of a right quality.

REFERENCE

(1) *Leistner, L. Wirth F.;* Die Fleischwirtschaft *17*, 803 (1965)

MEGFIGYELÉSEK HÚSIPARI TERMÉKEK REDOXIPOTENCIÁLJÁNAK MÉRÉSÉRŐL

W. Uchman és J. Gracz

Vizsgálataik célja különféle húsipari termékek redoxipotenciáljának mérésere szolgáló módszer kidolgozása volt. Megállapították, hogy erre a célra az rH érték mérése a legalkalmasabb. A mérést különböző elektródkombinációk segítségével (kalomel, üveg, platina elektródokból álló elektródpárokkal) végzik, egy különleges kapcsoló berendezés útján, amelyet erre a célra szerkesztettek laboratóriumukban és amely lehetővé teszi, hogy egyidejűleg nagyszámú mérést végezzenek, mert egy-egy mérés csak 10–15 másopercnyi időt igényel. A kapcsoló lehetővé teszi továbbá, hogy olyan laboratóriumokban is végezzenek megfigyeléseket, ahol csak egyetlen mérőműszer áll rendelkezésre.

О НАБЛЮДЕНИЯХ ИЗМЕРЕНИЙ ОКИСЛИТЕЛЬНО-ВОСТАНОВИТЕЛЬНОГО ПОТЕНЦИАЛА В ПРОДУКТАХ МЯСНОЙ ПРОМЫШЛЕННОСТИ

В. Ухман и Й. Грац

Целью исследования служила разработка метода для измерения окислительно-востановительного потенциала в разных продуктах мясной промышленности. Афторы установили, что для этого самым подходящим является измерение значения rH. Измерение производится помощью разных электрокомбинаций (парами электрод состоящихся из электродов каломелы, стекла и платины) путем одного специального включатель сконструированного для этой цели в лаборатории, при помощи которого представится возможность одновременно проводить больше измерений, так как продолжительность одного измерения составляет всего 10–15 секунд. Этим включателем имеется возможность проводить измерения в лабораториях где имеется в распоряжении только одно оборудование.

BEOBACHTUNGEN ÜBER DIE MESSUNG DES REDOXPOTENTIALS VON VERARBEITETEN FLEISCHPRODUKTEN

W. Uchman und J. Gracz

Die Untersuchungen bezweckten die Entwicklung einer Methode zur Messung des Redoxpotentials von verschiedenen Produkten der Fleischindustrie. Es wurde festgestellt, dass sich zu diesen Zweck die Messung des rH-Wertes am besten eignet. Die Messung wird mit verschiedenen Elektrodenkombinationen (mittels Elektrodenpaaren aus Kalomel-, Glas- und Platinelektroden) durch eine besondere Schalteinrichtung durchgeführt, die in ihrem Laboratorium gerade zu diesem Zweck konstruiert wurde und die die gleichzeitige Durchführung von vielen Messungen ermöglicht, weil eine Messung nur 10–15 Sekunden beansprucht. Die Schalteinrichtung ermöglicht ferner, dass man auch in solchen Laboratorien messen kann, wo nur ein einzelnes Messinstrument zur Verfügung steht.