Acta Alimentaria, Vol. 31 (2), pp. 99–123 (2002)

ON EVALUATION AND COMPARISON OF MEASUREMENT METHODS WITH SPECIAL REFERENCE TO THE MEAT AND MEAT PRODUCTS
A review

L. KÖRMENDY* and E. ZUKÁL

Hungarian Meat Research Institute, H–1097 Budapest, Gubacsi út 6/b. Hungary

(Received: 3 August 2000; revision received: 5 November 2001; accepted 14 November 2001)

The authors discuss the main systematizing principles, not generally used in the field of meat science, regarding critical appreciation and comparison of measurement methods. The presentation of some basic considerations is followed by the discussion of interfering factors. Besides the random error, the role and importance of the constant, proportional and random biases are also treated. The random error is related to the method, while the random bias is related to the test material. A clear distinction is necessary between deterministic and stochastic relations when various methods are compared, emphasizing a possible instability of the regression constants in the latter case. A number of examples are listed for both types of relation. The use of the correlation coefficient may be erroneous in comparing two methods. However, Mandel's sensitivity ratio often furnishes an appropriate basis of comparison. For better understanding, the considerations on biases are illustrated by a simplified example.

Thereafter, the authors deal with the most important view-points in developing and revising a method of measurement: simplicity, robustness and instability. The handling of extreme observations or outliers and the concentration dependence of the relative standard deviation (coefficient of variation) of measurement are also discussed.

Keywords: mathematical-statistical methods, analysis of meat and meat products, theory of measurement methods

As it is generally known, whenever a problem involves the use of data which are subject to dispersions, mathematical-statistical methods offer the only sound and logical means of their treatment and there is no alternative which is equally satisfactory. The ever increasing importance of measurements has created the need for a science of data analysis and this paper is an attempt to contribute to this task by presenting an overview on it, with special reference to meat and meat products. Alternative methods, which are simpler, faster attract interest and deserve attention. (Methods developed for scientific investigations do not pertain to this category). A need for such methods arises frequently, among others, in the on-line process control [QACCP: quality analysis and

* To whom correspondence should be addressed.
E-mail: OHKI@MAIL.INTERWARE.HU

0139-3006/2002/$ 5.00

critical control points (ERDŐS, 1998)]. In general, meat scientists are familiar with statistical techniques, though they often think that routine-like application of classic regression analysis provides sufficient information concerning the accuracy of the method in question. However, as shown in this paper, the instability of a calibration curve is often the crucial problem which may make a substitute method unreliable. We also believe that some systematizing principles, e.g. LAWTON and co-workers' (1979) concept of the constant, proportional and random biases, can help in the critical appreciation and comparison of methods.

1. Some general principles

The investigated test material has a **true** water, sodium, nitrite, nitrate, glucose, lactic acid etc. content (x_t) to be determined. The value obtained by the measurement will be denoted with x_m. In this case, the notion 'true value' seems to be clear and unequivocal.

However, it is not quite unequivocal when one talks about 'true fat content,' 'true protein content' in the case of meat and meat products. Namely, the meaning of 'fat' (occasional presence of free fatty acids and other fat decomposition products, presence of lipoproteins, phospholipids etc., ARNETH, 1998) and 'protein' (presence of peptides, free amino acids and other NPN-compounds) are contestable. Thus, it is more expedient to talk of 'ether extractable fraction', 'crude protein content', etc. The measured value depends here to a greater extent on the applied method. Thus, the specification of the applied method is of great importance in this case. Such methods are often **standardized** and are considered, by convention, as **reference** or **referee** methods, often serving as basis of comparison with so-called **substitute (surrogate)** methods. The value measured by the reference method will be denoted by x_r, and the use of the notion 'true reference value' (x_{rt}) is appropriate here. As discussed later, the true value can often be approximated by replicate ('parallel') measurements.

It is still more uncertain to talk about 'true tenderness', 'true colour value' etc. by the sensory assessment of meat and meat products, often performed by a testing panel with the help of a hedonic scale. It should be noted that the substitution of the sensory analysis by a simpler and faster physical method is justified only, if the physical method is closely correlated with the sensory test. In the latter case different theoretical considerations have to be applied as above; these will not be treated here.

2. The role of random error

'If the process does not respond to any property other than the one it is intended to measure' (WERNIMONT, 1987), then the applied method of measurement is **selective** (also called **specific**). Moreover, if the measured characteristic (e.g. absorbancy, weight of the sediment by gravimetric analysis etc.) is proportional (or is in a very close relationship) to the amount of the substance to be determined (analyte) in the test

material, the method is **quantitative.** However, the measured value (x_m) will often differ from the true one (x_t):

$$x_m = x_t + \delta \quad (1)$$

consequently

$$\delta = x_m - x_t,$$

where δ is the random error of the measurement caused by environmental, say, laboratory conditions (errors caused by weighing, pipetting, diluting the sample, by checking the colour transition of the indicator at titration etc.). Note that the δ-values may have positive or negative signs. They often have approximately normal distribution with finite variance $V\{\delta\}$, and expected value of zero.

If the mean, $\bar{x}_m$, of replicate measurements, carried out on the same well-homogenized test material is available:

$$\bar{x}_m = x_t + \bar{\delta} \quad (2)$$

consequently

$$\bar{\delta} = \bar{x}_m - x_t,$$

where $\bar{\delta}$ is the mean of the random errors of k replicate measurements.

It is not self-evident that a series of a random variable, like $\bar{\delta}$, converges necessarily to a constant value. However, neglecting theoretical details, we can say that the conditions for convergence are fulfilled in this special case. So, the random error $\bar{\delta}$ can be reduced ad libitum by taking the mean of numerous replicate measurements, carried out on the well-homogenized test material (also called sample unit or item), i.e. it converges to zero for increasing values of k,

$$k \to \infty, \quad \bar{\delta} \to 0, \quad \bar{x}_m \to x_t.$$

This is due to the fact that the square of standard error (variance) of $\bar{\delta}$ also tends to zero for increasing values of k,

$$V\{\bar{\delta}\} \to 0,$$

because

$$V\{\bar{\delta}\} = V\{\delta\}/k.$$

The above considerations also assume that x_m is **unbiased** (is free from systematic error), i. e. the inherent **method bias** and/or the **laboratory bias** are negligible (WERNIMONT, 1987).

It follows that

$$\sigma\{\bar{\delta}\} = \sigma\{\bar{x}_m\} = \sqrt{\frac{V\{\delta\}}{k}} = \sigma\{\delta\}/\sqrt{k} \quad (3)$$

As mentioned before, $V\{\delta\} = \sigma^2\{\delta\}$ is the variance (square of standard deviation) of δ, but also of x_m, because $V\{x_m\} = V\{x_t+\delta\} = V\{\delta\}$. For this reason, $\sigma\{\delta\}$ is also called standard deviation of the measurement method. (The true x_t value is, by definition, exempt from random error.)

In analytical practice, x_t is often replaced by a 'true' reference value (x_{rt}).

In a general sense, **trueness** refers to the absence of systematic error (bias), **precision** to the size of random error. The **accuracy** involves both trueness and precision (HOFMANN, 1987; INTERNATIONAL STANDARD, 1994; OLSEN, 1997).

It is relevant to note here that a clear distinction must be drawn between the dispersion of the individual values obtained from k replicate determinations being carried out on the **same** well-homogenized test material and the dispersion of the data obtained from n **different** test materials (often called sample units, items or less adequately 'repetitions').

The logical consequence which can be derived from Eqs. (1) and (2) can be seen in Fig. 1.

As generally known, according to the mathematical-statistical terminology, x_m or $\bar{x}_m$ are called **estimates** of x_t. According to Fisher, the convergence of the means to the true value x_t, as presented in Fig. 1, is called **consistent** estimation (HALD, 1964).

Note that the random error δ, of a particular measurement, i.e. the real departure of the measured value x_m, from the true value x_t (or from true reference value x_{rt}), is always unknown in practice. (Of course, if the actual value of δ were known, one could obtain x_t by correcting x_m with δ). However, the standard deviation of δ, ($\sigma\{\delta\}$), can be estimated with the help of replicate measurements. [In practice, with a finite number of replicates, one obtains $s\{\delta\}$, which is an **estimate** of $\sigma\{\delta\}$].

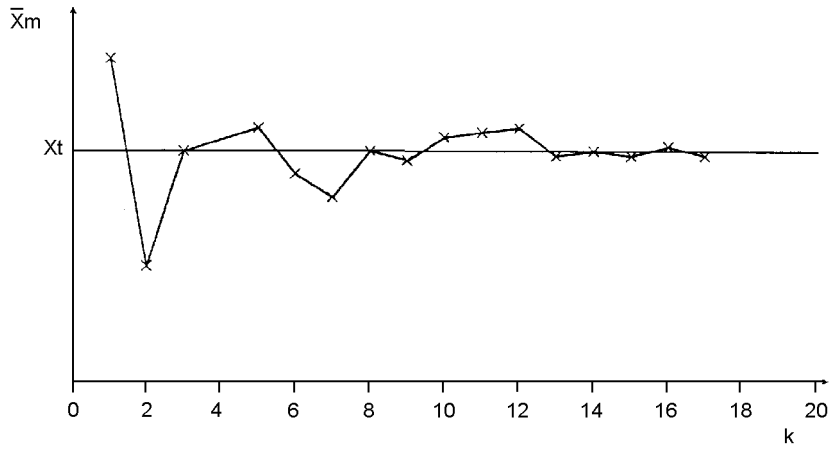

Fig. 1. Random fluctuation of the mean values of measurements ($\bar{x}_m$) about the true value (x_t) in function of the number of replicate determinations k, when the measured values are unbiased (free of systematic error). (Schematic presentation)

The statistical analysis has to be extended to the whole interval wherein the method in question is applicable. Therefore, in case of larger series of measurements, Eq. (1) takes the form:

$$x_{mi} = x_{ti} + \delta_i \quad (4)$$

for the sample unit with serial number i.

Here the relationship between x_m and x_t is evidently a proportional one and the proportionality factor (the slope of the straight line) equals unity, while the intercept (i. e. the value of x_m at $x_t = 0$) is zero. [It is naturally assumed that both variables (x_m and x_t) are expressed with identical numerical scales. Therefore, the **original** measured values (e.g. absorbancies) have to be converted accordingly (e.g. to concentrations)]. So the x_m values in Eqs (1), (2) or (4) also include the methodological calculations]. The relations represented by Eqs (1), (2) or (4), where the variability of x_m is due only to a random error δ, belong to the so-called **deterministic** relations.

3. The deterministic relations

The substitution of a reference method by a simpler, faster and/or less expensive substitute method causes less difficulties when the relation between the two methods is **deterministic**, i.e. data are subject to random errors only and the interfering factors are absent or, as discussed later, show constancy. Stable calibration (standard) curves can be obtained in these cases.

Consider the following examples for deterministic relations:

- Calibration curve of a spectrophotometric method: e.g. relation between the coloured substance and the measured absorbance.
- Methods for determining nitrite and total phosphorus content in meat products.
- Relation between density or refractive index and mass fraction in two-component systems (ethanol-water mixture, NaCl solutions etc.). However, if more than two components are present, influencing the density or the refractive index of the solutions, e.g. in liqueurs (containing also sugar), curing brines (containing also sugar and polyphosphates) etc. then, in general, the relations cannot be considered as deterministic.
- The laws of macrophysics.
- Determination of chloride ions in meat products by the Volhard's titrimetric method. Nevertheless, the Mohr's method does not belong to the deterministic relationships (VENEGAS & ANDÚJAR, 1979).
- Determination of Na and K in meats by flame-photometry.
- Relationship between the Soxhlet and the Foss-let methods for determining the crude fat content in meats (MIHÁLYI et al., 1981).

4. The role of interfering factors

Besides the random error, several other disturbing factors, called **interferences**, may also contribute to the results of measurements.

Consider the following examples for interferences:

- Some spectrophotometric methods, used formerly for the determination of glucose content in blood and not being selective enough, were disturbed by bilirubin and other blood constituents, also reacting with the respective colour forming reagents (KÖRMENDY & ZUKÁL, 1992). According to LAWTON and co-workers (1979), in principle, 200 various blood components may interfere in the determination of glucose.
- The presence of phosphates and gelatine in meat extracts reduces the clearness of colour transition of indicator by the argentometric titration of chloride ions (VENEGAS & ANDÚJAR, 1979).
- The biuret colour reagent is insensitive to the non-protein nitrogen (NPN) fraction in meat (MIHÁLYI, 1973). Moreover, the millimolar absorbancy indices (related to the N-content) of the connective tissue proteins as well as of the sarcoplasmic and myofibrillar proteins differ considerably. On the other hand, the Kjeldahl reference method, taken as basis of comparison, measures the NPN-content, too. These are sources of interference.
- According to GÁBOR (1983), the prediction of crude protein content in meat can be performed by measuring the absorbancy of tryptophan and tyrosine in the properly solved and diluted test material at 278 nm in the ultraviolet region. However, besides tryptophan and tyrosine, other substances in meat may also absorb light at 287 nm. Furthermore, the various protein fractions of meat have different tryptophan and tyrosine contents.
- All factors which influence – beside moisture, crude fat and crude protein – the near-infrared reflectance of meat, interfere in the determination of its proximate composition with the NIR-technique (NÁDAI & MIHÁLYI, 1984).
- Under the experimental conditions applied by NAGY and co-workers (2000), the determination of crude fat content in meat by the CW – NMR method is also influenced by the fatty acid composition of the fat in the test material.
- The measurement of the density of meat, for assessing its fat content, is also affected by the meat type as well as by its NaCl content, if salted (TIELMANN, 1991).
- As generally known, there is a close relationship between moisture, fat and protein content in fresh meat. Consequently, by determining one component (expediently the moisture or fat content), the other two components can be predicted with an acceptable accuracy. However, the dispersion of data about the regression line is not negligible (CALLOW, 1947).
- The polyphosphate and sugar content of the curing brine, if not measured separately, evidently interfere with the determination of NaCl content, estimated by density or refractive index. (The same is true for the determination of ethanol content in

liqueurs or other alcoholic beverages, containing also sugar and other contituents, if the latter components are not measured separately).

– The determination of the extent of heat treatment in canned picnics and hams by enzyme assays are disturbed by several factors. Apart from the temperature history of the product, the initial enzyme activity (before cooking), the pH-value, the NaCl and polyphosphate content, all influence the heat tolerance of the indicator enzyme in meat (KÖRMENDY et al., 1992). Further denaturation of the residual enzyme(s) may occur after heat treatment during long term frozen storage of the finished product (TOWNSEND, 1989).
– Although not pertaining to a classic analytical problem, the prediction of the lean content in pig carcasses by fat depth measurements is a spectacular example for the interference of numerous factors (DAUMAS & DHORNE, 1992).

5. The constant and/or proportional bias

For the sake of better understanding, the notion of the constant, proportional and random biases will be illustrated by a simplified example here.

Suppose we want to assess the total nitrogen content, x_T, of some type of cured and cooked meat product (e.g., canned picnics and hams), owing to its simplicity, by the biuret colour reaction (MIHÁLYI, 1973). Obviously, if the biuret colour reagent reacted with **all** nitrogen containing fractions in meat (sarcoplasmic, myofibrillar and connective proteins, non-protein nitrogen [NPN]) and if the millimolar absorbancy indices (related to nitrogen) were the same for all these fractions, then the relationship between the measured x_m and the true x_T-value would be for the i-th sample unit as follows:

$$x_{mi} = x_{Ti} + \delta_i \tag{5}$$

where δ is the random error of the measurement.

However, as MIHÁLYI (1973) pointed out, the biuret reagent is insensitive to the NPN-fraction (x_{NPN}), representing about 10–12% of the total nitrogen content (x_T) in fresh meat. So, it only reacts with the 'pure protein' fraction. For the sake of simplicity, let us assume that the millimolar absorbancy indices (related to nitrogen) are the same for all types of 'pure proteins' in meat. (In reality, the latter assumption is unfortunately not true). Moreover, the NPN-content is not measured separately. Consequently, $x_m<x_T$, and

$$x_{mi} = x_{Ti} - x_{NPNi} + \delta_i \tag{6}$$

Let us further assume now that the NPN-content, x_{NPN}, is the **same** (a_{NPN}) in all units of the meat product of interest (see Fig. 2A). In this fictitious case,

$$x_{mi} = x_{Ti} - a_{NPN} + \delta_i \quad (7)$$

where a_{NPN} is called **constant bias** (YOUDEN, 1951; LAWTON et al., 1979). The constant bias, if known, can be taken as correction and the total nitrogen content ($x_T+\delta$) can be assessed.

The next assumption concerns the constancy of the NPN/total nitrogen-ratio ($x_{NPNi}/x_{Ti} = c$, consequently: $x_{NPNi} = c \cdot x_{Ti}$). Therefore

$$x_{mi} = x_{Ti} - x_{NPNi} + \delta_i = x_{Ti} - c \cdot x_{Ti} + \delta_i$$

consequently,

$$x_{mi} = (1-c) \cdot x_{Ti} + \delta_i = b \cdot x_{Ti} + \delta_i \quad (8)$$

The departure of b from unity, 1-b = c (see Fig. 2B) is called **relative** or **proportional bias** (YOUDEN, 1951; LAWTON et al., 1979). (In this example, $0<c<1$ and if b equals unity, no proportional bias exists).

The **constant** and the **proportional biases** constitute the **deterministic** bias (called fixed bias by LAWTON and co-workers, 1979). If both types of bias are present (see Fig. 2C), the relationship will be as follows:

$$x_{mi} = b \cdot x_{Ti} - a_{NPN} + \delta_i$$

or in a general form

$$x_m = a + b \cdot x_t + \delta \quad (9)$$

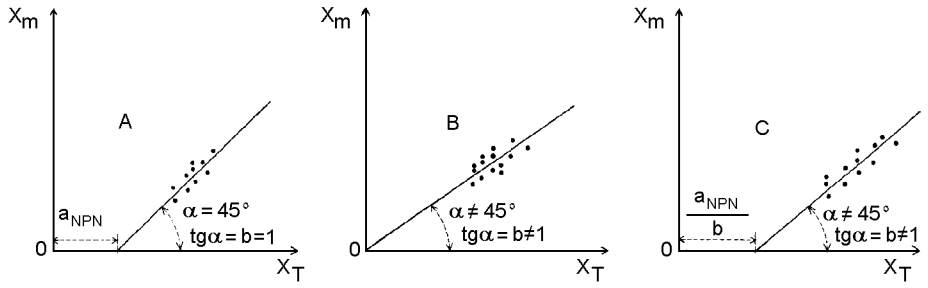

Fig. 2. Schematic presentation of the linear relationships between the measured biuret value (x_m) and total nitrogen content (x_T) in meat when the bias (caused by the presence of NPN in meat) is deterministic. [2A: $x_{mi} = x_{Ti} - a_{NPN} + \delta_i$ (constant bias). 2B: $x_{mi} = b \cdot x_{Ti} + \delta_i$ (proportional bias). 2C: $x_{mi} = b \cdot x_{Ti} - a_{NPN} + \delta_i$ (both types of deterministic biases are present)]. The dispersion of the data is only due to the random error. α denotes angle

Note that the deterministic bias, if known, can be used as correction factor for obtaining, in this example, unbiased estimates of the total nitrogen content, x_T,

$$x_{Ti} = \frac{x_{mi} + a_{NPN} - \delta_i}{b} \quad (10)$$

Relations (4) to (10) are all **deterministic**, since the only source of dispersion is the random error of measurement (δ) of the biuret method in the above example.

6. The random bias and the stochastic relations

Nevertheless, the NPN content and/or the x_{NPN}/x_T ratio are never constant in the meat or meat products, but are subject, from item to item, to random dispersions, i.e. they are random variables with **probability distributions**. The same phenomenon can be observed in most practical situations; in effect, the biases are not 'constant'. In these realistic circumstances, the former **deterministic** relations [see, e.g. Eq.(9)] are no more valid and, simplifying the mathematical background of the problem, the general form of the appropriate relationship can be written for the i-th sample unit as follows:

$$x_{mi} = a + b \cdot x_{ti} + \delta_i + e_i \tag{11}$$

beside the **deterministic bias** (represented by the constants $a \neq 0$ and $b \neq 1$) and the random error (δ), a **random bias** (denoted by e) appears, too (LAWTON et al., 1979). Consequently, δ **is related to the method of measurement**, however, **e is related to the test material**.

If k replicate measurements are performed from the same well-homogenized sample unit, the sum of the random error and random bias (E) will be

$$E = \bar{\delta} + e \tag{12}$$

$\bar{\delta}$ and e being stochastically independent, their variances are additive:

$$V\{E\} = V\{\bar{\delta}\} + V\{e\} = V\{\delta\}/k + V\{e\} \tag{13}$$

As Eq. (13) shows, for increasing number of replicate ('parallel') measurements (k), only the variance of the random error will be reduced. However, the variance of the random bias **remains unchanged**. Thus, Eq. (11) represents, according to the mathematical statistical terminology, a **stochastic** relationship. So, we have two predictable sources of error characterized by the constants a and b, and two unpredictable random sources of error characterized by $V\{\delta\}$ and $V\{e\}$ (LAWTON et al., 1979).

When the variance of the random bias is much larger than the variance of the random error,

$$V\{e\} >> V\{\delta\}$$

an increase of the number of replicate determinations does not improve the precision of the measurement. For reducing the random bias, the **mean** of a random sample of size n has to be taken. In this case,

$$V\{\bar{e}\} = V\{e\}/n \tag{14}$$

consequently, if $n \to \infty$, $V\{\bar{e}\} \to 0$ and $\bar{e} \to 0$ [see remark below Eq. (2)]. Furthermore,

$$V\{\bar{E}\} = V\{\delta\}/k \cdot n + V\{e\}/n \quad (15)$$

For this reason, the method in question, even if rapid, simple or less expensive, may be inappropriate in practice, since the requirement for accuracy is generally related to a given test material and not to the **mean value** of numerous test materials. (We could mention here, as a typical example, the methods used in laboratory diagnostics.)

Considering Eqs. (5) to (10), it can be concluded that, taking the above example, if the relation between the biuret and Kjeldahl method were **deterministic,** the units in the 'population' having the same total N-content, would also have the same NPN-content. The dispersion of the data here would be due solely to the random error of the method of measurement (δ), the latter one being the biuret method in this unreal case. On the other hand, in case of a **stochastic** relationship, the units in the 'population' that have the same total N-content, have more or less different NPN-contents. The latter assumption corresponds here to the reality.

The previous simplified example serves for interpretation of the concept of the deterministic ('fixed')and random biases. It is obvious that these considerations can be generalized for similar problems.

This paper does not involve the mathematical statistical problems of multivariate calibration, where two or more explanatory variables are present. This area has an abundant literature. We only refer here to the book edited by PIGGOTT (1986).

7. The effect of the dispersion of interfering factors on the reliability of measured values

As mentioned previously, the x_{NPN}-value, as a random variable, changes from item to item and therefore introduces a random bias in the relationship between x_m and x_T. So, the x_{NPN}-values, as all other random variables, have a probability distribution.

Suppose the distribution of x_{NPN} (pertaining to a given x_T-value) is approximately normal, with mean $\bar{x}_{NPN,}$ and standard deviation $\sigma\{x_{NPN}\}$.

Let us further assume that, owing to a systematic change in the processing conditions (e.g. increase of the time of conditioning of cured hams, resulting in a more intensive proteolysis), these means, $\bar{x}_{NPN}$, have been shifted, without change in standard deviation, ($\sigma\{x_{NPN}\}$), according to Fig. 3. The consequence of this shift, as a typical mark of instability of the relation of x_{NPN} with x_T, can also be seen in Fig. 3.

However, as shown in Fig. 4, the standard deviation $\sigma\{x_{NPN}\}$ may also change without change in the intercept and slope of the relation between x_{NPN} and x_T. Its consequence is the greater dispersion of the data about the calibration curve, reducing the precision of estimation. The **lack of stability** is also evident here.

A more complex situation arises when the mean, the standard deviation and the **shape** of the distribution are all changing simultaneously (Fig. 5). [As generally known, a polymodal distribution (with two or more peaks) points to the presence of an **unstable** heterogeneous population (HALD, 1964)].

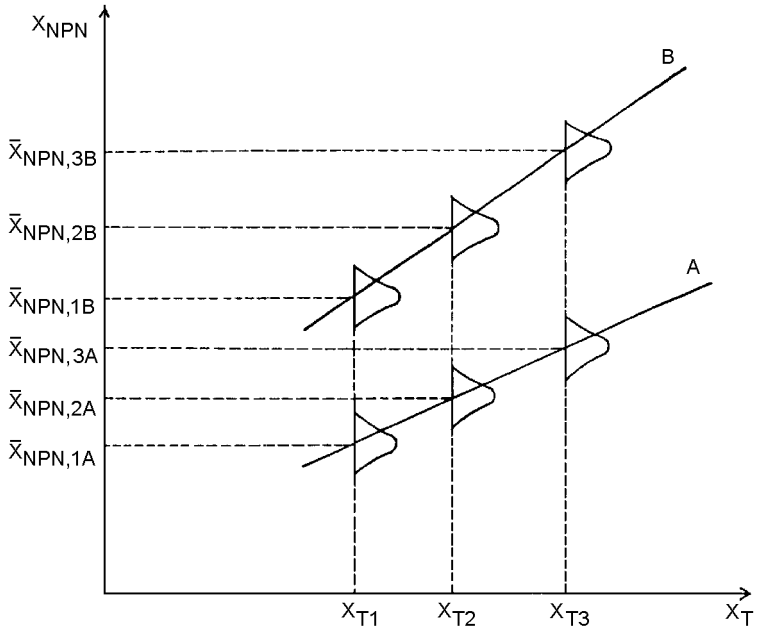

Fig. 3. The effect of the shift of distribution of NPN-content in the meat product of interest on the relation of x_{NPN} with x_T, without change in standard deviation. (A = original state, B = modified state)

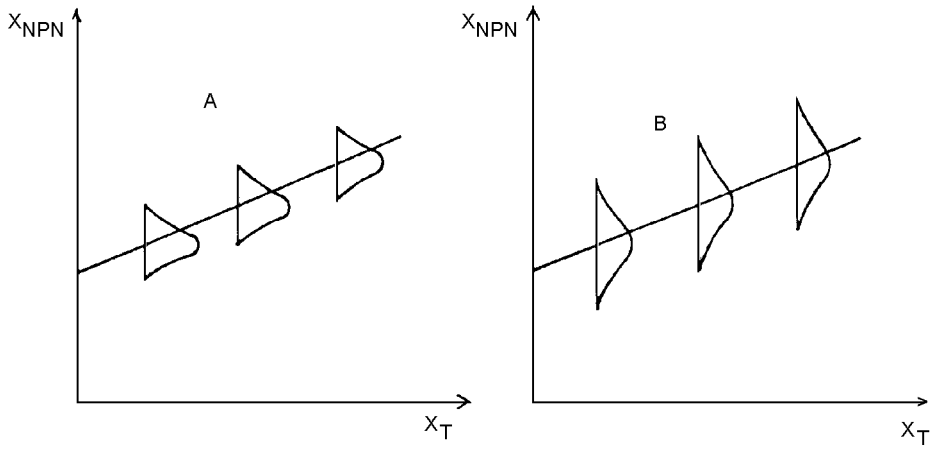

Fig. 4. The effect of the increase in standard deviation $\sigma\{x_{NPN}\}$ on the dispersion of data about the relation of x_{NPN} with x_T, without change in the intercept and slope. (Schematic presentation. A = original state, B = modified state)

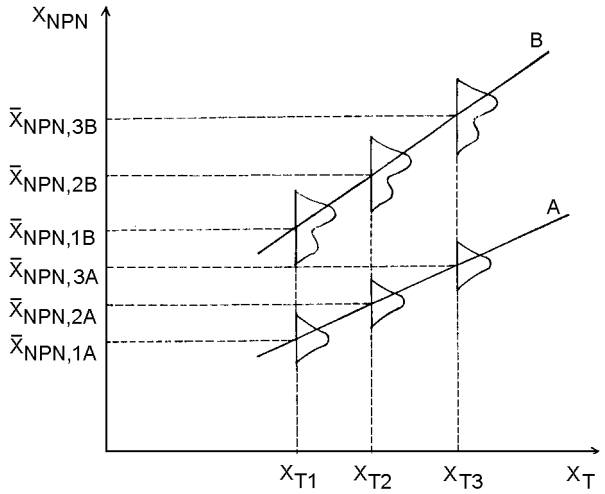

Fig. 5. Simultaneous shift of the mean, standard deviation and shape in the distribution of x_{NPN}. (Schematic presentation. A = original state, B = modified state)

In practical work, the true total nitrogen contents (x_T) of the items are always unknown and are usually determined with the Kjeldahl reference method (x_r) during the calibration procedure. In this way, instead of x_T, x_r has to be substituted into Eq. (11) and, in principle, the random error of the Kjeldahl reference method should also be taken into account.

Thus, in the case of a specified meat or meat product, for a successful substitution of the Kjeldahl reference method by the simpler biuret substitute method, the following requirements should be considered:

– Both the Kjeldahl and the biuret methods, concerning the random errors, have to possess a fair degree of precision;
– the shape of distribution of the NPN-content (for any given x_T-value) must be unimodal (though not necessarily normal);
– the standard deviation of the distribution of NPN-content or, the standard deviation of the distribution of the respective random bias, which is the same, must be adequately low;
– although x_{NPN} is variable, its distribution must be **stable**, that is, the mean, the standard deviation and the shape of the distribution must be constant. The possible causes of instability have been presented formerly.

As shown in Fig. 6, the requirement for stability is **not** accomplished with the biuret method (KÖRMENDY et al., 1981). It is to be emphasized that the determination of the relationship between the biuret and the Kjeldahl method is used for a **calibration (standard) curve of a stochastic relation**. The repetition of the calibration procedure resulted here, for not quite revealed reasons, in two very different lines (Fig. 6).

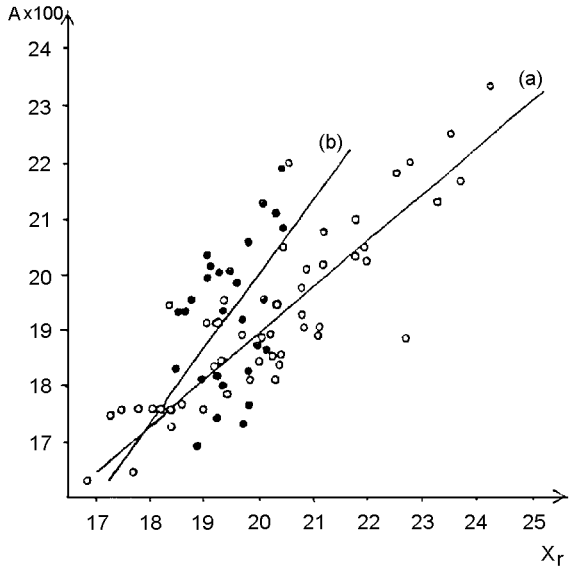

Fig. 6. Comparison of the Kjeldahl reference method (x_r = N·6.25) with the biuret one in canned ham (A = absorbancy at 540 nm). (a) = first calibration, (b) = second calibration. n_a = 49; n_b = 28

Obviously, in the case of a **stochastic** relationship, the calibration (standard) curve must be prepared with various and numerous sample units. On the other hand, if the relationship between the examined methods is **deterministic**, the calibration curve can be set up by preparing a series of dilution from the same stock solution or often from the same well-homogenized sample unit. For the above reasons, the analyst should be very cautious and circumspect, if the relationship between the methods to be compared is not deterministic, but **stochastic.** (Generally simpler, faster, less expensive, chemical or physical methods are compared with reference [standard] methods). Steady 'recalibrations' are not always practically possible and do not put an end to the uncertainty. In the majority of cases, the analyst is unaware of the fact that the distribution of the interfering factor(s) has changed in the 'population'. [Note that **analysis of covariance** is the appropriate method for comparing various calibration curves (DIXON & MASSEY, 1957)].

In order to obtain more 'security', the instinctive reaction of the analyst is often to increase the sample size for the establishment of the calibration curve. However, in the case of instability, this procedure does not help. Any systematic change in the conditions, as in the example above, may alter the original calibration curve. For this reason, a careful, systematic examination of all potential interfering factors of the substitute method has to precede always the collection of data for the setting up of a calibration curve. Such methods are mostly suited, under standardized conditions, for the on-line production control, but are less appropriate for official quality inspection.

Unfortunately, in practice, not only one, but numerous interfering factors affect the accuracy of a method of measurement. Evidently, the situation will be more complex, when the effect of the interfering factor(s) is not additive and **interactions** are also present (e.g. formation of new substances disturbing the colour reaction, their effect on the rate of colour formation etc.).

8. Comparison of two deterministically related methods

Eq. (9) presents the linear deterministic relationship between the measured and the true value in a general form. However, in practice the true value, x_t, which is, by definition, exempt from random error, is often unknown and only the measured values of the methods to be compared are available. In comparing two methods, the deterministic relation between results of the random error-free 'y' method, y_t, and of the random error-free 'x' method, x_t, will be,

$$y_{ti} = A + B \cdot x_{ti} \tag{16}$$

regarding a sample unit with serial number i.

The values of the constants (assuming that both x and y are expressed with identical numerical scale), depend on the presence and size of the deterministic bias [see also Eq. (9)].

However, the random measurement errors cannot be neglected

$$x_i = x_{ti} + \delta_i$$

and

$$y_i = y_{ti} + \varepsilon_i$$

If the number of replicate measurements increases; $k_\delta \to \infty$ and $k_\varepsilon \to \infty$, the variances of the means of δ and ε, $V\{\bar{\delta}\}$ and $V\{\bar{\varepsilon}\}$ converge to zero.

When both variables ('x' and 'y') are loaded with random errors, the estimates α and β of A and B in Eq. (16) have to be obtained, for a sample of size n, with the help of Deming's regression equation (MANDEL, 1964). Namely, in this case, the classic regression formulae, which implicitly assume that the 'x' variable is exempt from random error, cannot be applied correctly (see also KÖRMENDY et al., 1989).

$$\hat{y}_i = \alpha + \beta \cdot \hat{x}_i \tag{17}$$

where $\hat{y}$ and $\hat{x}$ are Deming's regression estimates of the respective variables,

$$\alpha = \bar{y} - \beta \cdot \bar{x} \tag{18}$$

$$\bar{y} = \Sigma y_i / n \quad \bar{x} = \Sigma x_i / n$$

$$\beta = \frac{\lambda \cdot w - u + [(u - \lambda \cdot w)^2 + 4\lambda \cdot p^2]^{1/2}}{2\lambda \cdot p} \quad (19)$$

$$\lambda = \frac{V\{\delta\} / k_\delta}{V\{\varepsilon\} / k_\varepsilon} \quad (20)$$

$$p = \Sigma x_i y_i - \Sigma x_i \cdot \Sigma y_i / n$$

$$u = \Sigma x_i^2 - \frac{(\Sigma x_i)^2}{n}$$

$$w = \Sigma y_i^2 - \frac{(\Sigma y_i)^2}{n}$$

k_ε and k_δ are the number of replicates with methods 'y' and 'x', respectively. [It is assumed here that the same number of replicates is used with each sample unit, however, k_ε and k_δ may be different. In the latter case, another formula has to be applied for the k-values in Eq. (20) which is not presented here (WEBER, 1978)].

For calculatig β, the value of λ has to be known in advance or $V\{\varepsilon\} = s^2\{\varepsilon\}$ and $V\{\delta\} = s^2\{\delta\}$ should be estimated from an adequate number of replicate measurements carried out on each well homogenized test material (sample unit) during the calibration procedure. (The authors send readily a practical example for those readers who want to get acquainted with the details of the above calculation).

It can be demonstrated that the consequence of $V\{\delta\} = 0$ is, $\lambda = 0$ and Eq. (19) will be reduced to the classical form $\beta = p/u$ as presented in mathematical statistical books. Note that the interchange of x with y in Eq. (17) gives the reciprocal of β ($\beta' = 1/\beta$). As known, the classic regression analysis gives two regression lines; $\beta' \neq 1/\beta$.

9. Comparison of two stochastically related methods

In this case, first a reference method ('x_r') has to be assigned. As basis of comparison, the results obtained with the reference method are taken always to the abscissa, and by definition unbiased, i.e. they are subject only to random error. This is because, in principle, a biased method cannot serve for basis of comparison. Thus, the relationship between the measured (x_r) and the true (x_{rt}) values is the following. For the i-th sample unit:

$$x_{ri} = x_{rti} + \delta_i$$

On the other hand, in the case of a stochastic relation, the method to be compared, called here as substitute method ('y_S'), is subject, besides the random error (ε), to a random bias (e), too. Therefore,

$$y_{si} = \bar{y}_{sti} + \varepsilon_i + e_i$$

where $\bar{y}_{sti}$ is the 'true' mean value of the substitute method for given $x_{rti.}$ The linear regression equation is as follows:

$$\hat{y}_{si} = \alpha + \beta \cdot \hat{x}_{ri} \tag{21}$$

where $\hat{y}_s$ and $\hat{x}_r$ denote Deming's regression estimates of the respective variables.

The ratio of the respective variances is

$$\lambda = \frac{V\{\delta\} / k_\delta}{V\{e\} + V\{\varepsilon\} / k_\varepsilon} = \frac{V\{\bar{\delta}\}}{V\{e\} + V\{\bar{\varepsilon}\}} \tag{22}$$

It is evident that λ is unknown in advance in this case, since, contrary to $V\{\varepsilon\}$ and $V\{\delta\}$, $V\{e\}$ cannot be obtained from replicate measurements. So, Eq.(19) is not suited for calculating β. Nevertheless, FÉNYES and co-workers (1970) have found the appropriate formula:

$$\beta = \frac{p}{u - (n-2) \cdot V\{\delta\} / k_\delta} \tag{23}$$

So, it is sufficient to know only the variance of δ, i.e. the variance of the referee method ('x') from replicate measurements, when using Eq. (23).

The total variance of $e+\bar{\varepsilon}$ obtainable from the calculation at the calibration procedure is as follows:

$$V\{e + \bar{\varepsilon}\} = V\{e\} + V\{\varepsilon\} / k_\varepsilon = \frac{w - \beta \cdot p}{n-2} \tag{24}$$

which means that only the $V\{\varepsilon\}/k_\varepsilon = V\{\bar{\varepsilon}\}$ value can be reduced ad libitum by increasing the number of replicate measurements (carried out on each well homogenized test material) with the substitute method. However, $V\{e\}$, which is related to the test material, remains unchanged [see also Eq. (13)]. If $V\{\varepsilon\}$ is known in advance, $V\{e\}$ can be obtained from Eq. (24), while α is calculated by Eq. (18). The variances of α and β can be obtained by the formulae of FÉNYES and co-workers (1970).

The reader can be acquainted with the details of these calculations through an example in a previous paper (KÖRMENDY et al., 1989).

10. Tests of significance of the constants in the linear regression equation

It is interesting to know whether the intercept a is significantly different or not from zero and b significantly different from 1. The latter is mainly important when both variables are expressed with identical numerical scale. Namely, in this case, the presence or absence of the deterministic bias can be assessed. Starting, in a general sense, from a linear relation: $Y = A+B \cdot X$, three hypotheses may have importance:

$$Y = B \cdot X \quad (A = 0)$$
$$Y = X \quad (A = 0 \text{ and } B = 1)$$
$$Y = A + X \quad (A \neq 0 \text{ and } B = 1)$$

If the two methods to be compared do not coincide, i.e. the hypothesis $Y = X$ does not hold, the causes have to be revealed, if possible.

This calculation procedure is accessible in a previous publication (KÖRMENDY et al., 1989) and is not presented here.

11. The correlation coefficient is not appropriate for comparing two methods

Although generally used, the correlation coefficient (R) is not informative in a comparison of two methods. This can be verified easily by examining the behaviour of the (unadjusted) coefficient of determination (R^2):

$$R^2 = 1 - \frac{(n-2)\cdot s^2\{y,x\}}{(n-1)\cdot s^2\{y\}} \tag{25}$$

where $s^2\{y,x\}$ is the variance about the regression line and $s^2\{y\}$ is the total variance of all y values.

In general, collection of experimental data for setting up a calibration curve is performed in an arbitrary way. For instance, in comparing two methods for the determination of crude fat content in meat, items with low, medium and high fat contents are arbitrarily selected from the 'population'. Thus, the applied model is rather a 'functional' than a 'structural' one (FULLER, 1987). (The 'structural' model would mean a random selection of the items from the 'population'). However, the magnitude of $s^2\{y\}$ highly depends on how the y-values, i.e the fat contents of the items submitted to analysis, are distributed over the total range of variation. On the other hand, $s^2\{y,x\}$ is principially invariant with respect to the actual fat contents of the items. Consequently, R^2 can also be altered arbitrarily with the suitable choice of items, if these items are not taken randomly from the 'population' (Fig. 7). The same is true, e.g. in evaluating the calibration curves of spectrophotometric methods (absorbancy vs. concentration).

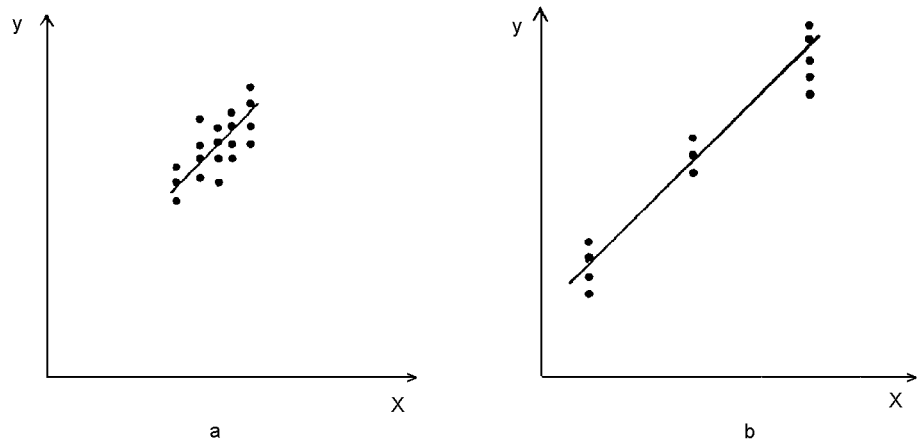

Fig. 7. Schematic presentation of the dispersion of data for low (a) and high s{y} values (b).
a: low correlation coefficient, b: high correlation coefficient [see also Eq. (25)]

12. The concept of sensitivity ratio

Mandel's sensitivity ratio is a simple but very valuable tool in comparing two methods (MANDEL, 1964).

The sensitivity ratio of method 'y' with respect to method 'x' is as follows:

$$S\{y / x\} = \frac{|dy / dx|}{s\{e + \bar{\varepsilon}\} / s\{\bar{\delta}\}} \tag{26}$$

where |dy/dx| is the absolute value of first derivative of y vs. x, $s\{e+\bar{\varepsilon}\}$ and $s\{\bar{\delta}\}$ are the standard errors of the 'y' and 'x' methods, respectively. [$s\{e+\bar{\varepsilon}\}$ is the square root of Eq. (24)]. Eq. (26) is an extension of the original MANDEL's (1964) formula, taking into account the effect of random bias as well as the possible reduction of ε and δ by replicate measurements. MANDEL's (1964) original equation has been defined for the special case when e = 0 and $k_\varepsilon = k_\delta$, i.e. only for deterministic relationships:

$$S\{y / x\} = \frac{|dy / dx|}{s\{\varepsilon\} / s\{\delta\}}$$

Substituting λ into Eq. (26),

$$S\{y/x\} = |dy/dx| \cdot \sqrt{\lambda} \tag{27}$$

where λ can be calculated from Eq. (20) or (22) for determininistic or stochastic relationships, respectively.

In the linear case

$$S\{y/x\} = |\beta| \cdot \sqrt{\lambda} \tag{28}$$

If the relationship between the methods to be compared (y vs. x) is not linear, S{y/x} may be dependent of x. It may happen that in a given interval method 'x' is more sensitive than method 'y' (S{y/x}<1), but in another one it is reversed (S{y/x}>1) (see Fig. 8). If S{y/x} = 1, both methods are equally sensitive.

The sensitivity ratio is invariant with respect to any transformation of scale.

Note that, if the x-vales are practically error-free, they represent the 'true' values, S{y/x} = 0. In such a case, the size of $\sqrt{V\{\varepsilon\}}$ or $\sqrt{V\{e+\bar{\varepsilon}\}}$ serves for the assessment of the precision of method 'y' or 'y_s'.

It can be demonstrated that in case of a **deterministic** relationship (V{e} = 0), S{x/y} = 1/S{y/x}. However, if the relation between the methods to be compared is **stochastic** (V{e} > 0), then S{x/y} ≠ 1/S{y/x}!

The details for calculation of S{y/x} have been presented in a previous paper (KÖRMENDY et al., 1989).

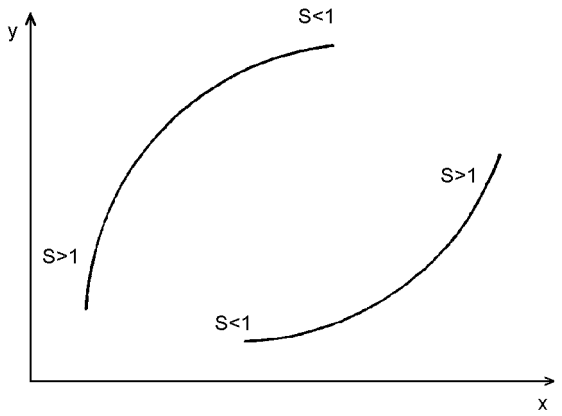

Fig. 8. Change of sensitivity ratio (S) in non-linear cases, for constant λ. (Schematic presentation)

13. What are the most important view-points in developing a method of measurement?

According to YOUDEN & STEINER (1975) and WERNIMONT (1987), the other performance characteristics of a method, besides accuracy and specifity (selectivity) are as follows:

- Ruggedness (robustness) means that the method withstands small uncontrolled changes in its operating conditions.
- Practicability means that the process requires no extraordinary (and often very expensive) instruments, reagents etc., so it is appropriate for routine control work in a regular laboratory.
- Lowest limit of reliable measurement, i.e. the lowest level of the property being measured, which can be reliably distinguished from zero.

It is relevant to note here that the **method to be developed should be as simple as possible**. As far as possible, one has to start with the simplest process. If it does not work, further operations should be included step by step. For instance, is the deproteinization of the meat extract in an analytical procedure by all means necessary? If yes, heat treatment of the meat slurry may often be sufficient; the use of a protein precipitating reagent can perhaps be avoided. In some cases, the nitrite content of curing brines can be determined by the Griess-colour reagent with acceptable accuracy, after a thousandfold dilution, without previous deproteinization (KÖRMENDY, 1958). The sarcoplasmic and mitochondrial GOT isoemzymes can be separated electrophoretically from the muscle press juice without previous purification on Sephadex-gel or by fractional precipitation with $(NH_4)_2SO_4$ (KÖRMENDY et al., 1965; HAMM et al., 1969).

It is always advisable to reconsider the necessity of each step of an existing method, when working on its critical revision. By analogy, the same way of thinking concerns the production processes. For example, NEMES (1966) demonstrated that the preliminary 'dripping' of meat pieces in the manufacture of salami could be omitted, the pre-cooking of liver was superfluous in the traditional liver sausage manufacturing process (MLYNARIK et al., 1964), as well as the crushing of meat (before mincing) in the bologna production process (KÁRPÁTI, 1956) etc.

As far as possible, the method to be elaborated should be **robust**. YOUDEN & STEINER (1975), as well as WERNIMONT (1987) present very useful experimental (fractional factorial) designs in their books for evaluating the ruggedness of an analytical process.

The contrary of robustness is **instability**. Figure 9 shows the colour development of a nitrite solution after addition of the Griess-reagent. It is obvious that, because of the steep rise of the absorbancy ($dA/dt >> 0$) up to nearly 40 min, the absorbancy readings are excessively time (and temperature) dependent in the first period. Therefore, as it is a general custom, the readings have to be done in the **near-stationary** second period ($t > 40$ min, $dA/dt \approx 0$). (The previous problem deserves special attention when using autoanalyser!). Naturally, this principle is valid for any step in the method of measurement: Dilution of 10 cm^3 to 100 cm^3 is more precise in a volumetric flask than 1 cm^3 to 10 cm^3. The use of pipettes with larger volumes is generally more accurate than the use of pipettes with small ones.

Generally, the simpler the method, the more robust. For instance, the determination of moisture content of meat by drying in an oven at 103 °C is more robust than the complicated Kjeldahl procedure or the phosphatase assay for controlling the extent of heating in canned picnics and hams (KÖRMENDY et al., 1992).

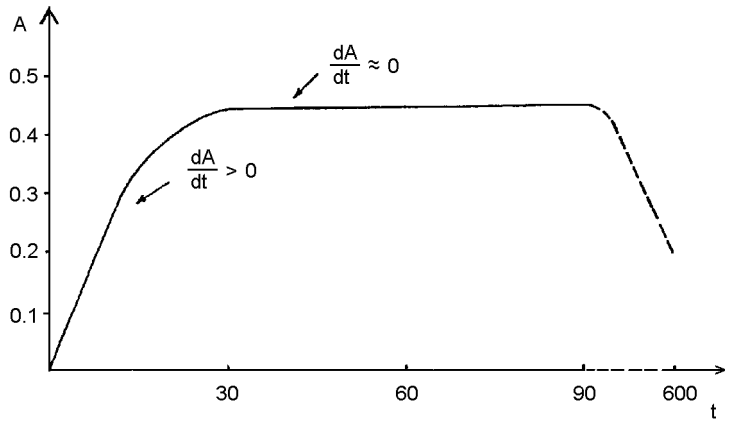

Fig. 9. Colour formation of the Griess-nitrite reaction in function of time at room temperature. (A = absorbancy, t = time in min. Schematic presentation)

Methods for determining sodium chloride, total phosphorus, nitrite and crude fat content in meat and meat products can be considered as robust. On the other hand, methods for determining the nitrate content by Cd-column, the ammonia content by distillation (after Kjedahl's digestion) or the peroxide value and TBA number belong to the less robust ones (A.O.A.C., 1998; GRAU, 1969). Needless to say that the meat researcher has to strive for developing, if possible, robust measurement methods.

14. The handling of extreme observations (outliers)

The question is often raised in practice whether or not certain values in a sample are **extreme observations,** often called **outliers**. Such outliers may occur because of invalid data resulting from gross errors or blunders. In this case, the outliers should be excluded from the calculations.

If not so, the presence of **true outliers** may result from the fact that the population contains a certain proportion of extreme cases, i.e. it is bimodal (or having more than two peaks; polymodal), representing an unstable, 'heterogeneous' population. However, first of all, we have to use a statistical test in order to be ascertained that the apparently extreme observations are really outliers, belonging to a distinct population. (Theoretically, extreme observations may occur, with low probability, in 'homogeneous' populations, too). Several statistical tests exist for this purpose, e.g. Grubbs test (A.O.A.C., 1995), Dixon test (ANON, 1983), which are not discussed here.

However, the existence of outlying observations is essentially not a mathematical statistical problem but a scientific one. Namely, what is the real cause of the 'heterogeneity' with regard to the property under study? We may eliminate the outliers from the calculation, but we cannot reject them as 'non-typical' values without any further theoretical or practical considerations. If we are unable to find, despite a profound scientific study, the cause of the presence of outlying observations, referring to an unstable 'heterogeneous', polymodal distribution in the population, it has to be mentioned in the paper or report. In this way, we do not mislead the reader.

15. Are the precision parameters of methods measuring different properties comparable?

As discussed previously, when the methods measure the same property, their comparison is a clear and unequivocal task. However, can we compare the precision of two methods measuring different properties? For instance, can we say that the Soxhlet method is more precise than the Kjeldahl one etc.?

At first, the question seems to be illogical. It is obvious that neither the standard deviation nor the dimensionless relative standard deviation [also called coefficient of variation (CV)] of the methods of interest are informative in this case because, among others, both precision parameters are concentration dependent (PÜSCHEL, 1968;

HORWITZ, 1982). Nevertheless, it would be completely unreasonable to refer, e.g. the protein and fat content in meat to the same concentration.

PÜSCHEL (1968) and HORWITZ (1982), collected large amount of micro- and macro-analytical data from different sources, representing a variety of analytes, matrices and measurement techniques. [PÜSCHEL's (1968) data cover a concentration range of 140 µg/kg to 995 g/kg]. They established a nearly linear tendency, with great dispersion about the regression line, between log CV and logarithm of concentration of the analysed substance (log x):

$$\hat{\log}\,CV = f - g \cdot \log x \qquad (29)$$

where f and g are the intercept and slope of the linear regression equation, respectively.

Consequently, the lower is the concentration of the analysed substance in the test material, the higher is, in tendency, its coefficient of variation. (Naturally, to any given x-value, different methods may have different expected CV-values).

In spite of the above interesting observation, giving an overall idea on the relation between analytical 'error' and analyte concentration, the acceptability of a method, with respect to its precision, cannot be assessed from the magnitude of standard deviation or relative standard deviation (CV) in itself. However, it has to be examined from the view-point of practical requirements, e.g. acceptable and tolerance quality levels, probability of the errors of first and second kind etc. in quality control systems (STEINER, 1967).

*

This research work has been sponsored by OTKA Bureau (Bureau of National Research Funds, Hungarian Academy of Sciences) under project number T 022231. The authors are very indebted to Dr. A. ITTZÉS and Professor I. KÖRMENDY for revising the manuscript.

Symbols

A: Intercept of the linear regression equation of the relation between variables with hypothetically true values. In Fig. 9, it denotes absorbancy

a: Constant bias in the linear relationship between the measured (x_m) and true (x_t) values

B: Slope of the linear regression equation of the relation between variables with hypothetically true values

1–b: Proportional bias in the linear relation between the measured (x_m) and true (x_t) values

c = 1–b

CV: Coefficient of variation, also called relative standard deviation [see Eq. (29)]

e: Notation for the random bias

f: Intercept of Eq. (29)

g: Slope of Eq. (29)

i: Serial number of the test materials (sample units, items) in the sample or in the 'population'

k: Number of replicate measurements

k_δ: Number of replicate measurements by the 'x' method or by the reference method ('x_r').[See Eqs. (20), (22) and (23)]

k_ε: Number of replicate measurements by the 'y' method or by the substitute method ('y_s').[See Eqs. (20) and (22)]

m: Subscript, refers to the measured value

NPN: Subscript, refers to non-protein nitrogen

n: Sample size

$p = \Sigma x_i y_i - \Sigma x_i \cdot \Sigma y_i / n$

r: Subscript, refers to the reference method

R: Correlation coefficient (R^2 = coefficient of determination)

s: Subscript, refers to the substitute method

s{ }: Standard deviation of the variable inside the parantheses in a sample of size n (s^2{ } = variance)

$s^2\{y,x\}$: Variance about the regression line

S{y/x} and S or S{x/y}: Sensitivity ratio of method 'y' with respect to method 'x' or inversely

t: Subscript, refers to the true value. In Fig. 9, it denotes time

T: Subscript, refers to the total nitrogen content

$u = \Sigma x_i^2 - (\Sigma x_i)^2 / n$

V{ }: Variance of the variable inside the parantheses

$w = \Sigma y_i^2 - (\Sigma y_i)^2 / n$

x: Variable referring to the corresponding method or concentration of the analysed substance in Eq. (29)

X: 'Explanatory' variable of a linear relationship in a general sense

y: Variable referring to the corresponding method

Y: 'Dependent' variable of a linear relationship in a general sense

α: Sample estimate of A with the help of DEMING's regression equation. Denotes angle in Fig. 2

β: Sample estimate of B with the help of DEMING's regression equation

δ: Random error of measurement in a general sense. In Eq. (20) it is related to the 'x' method and in Eq. (22) to the reference method ('x_r')

ε: Random error of measurement related to the 'y' method [see Eqs. (20)] and in Eq. (22) to the substitute method ('y_s')

$$\lambda = \frac{V\{\delta\} / k_\delta}{V\{\varepsilon\} / k_\varepsilon} \text{ or } \frac{V\{\delta\} / k_\delta}{V\{e\} + V\{\varepsilon\} / k_\varepsilon}$$

σ{ }: Standard deviation of the variable inside the parantheses regarding the 'population'

$\bar{x}$, $\bar{y}$, $\bar{\delta}$, $\bar{\varepsilon}$: denote mean values of the respective variables

$\hat{x}$ and $\hat{y}$: denote Deming's regression estimates of the respective variable

References

ANON (1983): Planung und statistische Auswertung von Ringversuchen. Amtl. Sammlung § 35 LMBG. *Statistik*, Mai, 1–17.

A.O.A.C. (1995): International guidelines for collaborative study procedures to validate characteristics of a method of analysis. *J. AOAC int., 78*, 143A–160A.

A.O.A.C. (1998): *Official Methods of Analysis of AOAC International*. AOAC International, Gaithersburg, USA. Ch 39.1.15–19; Ch 41.1.16.

ARNETH, W. (1998): Über die Bestimmung des intramuskulären Fettes. *Fleischwirtsch., 78*, 218–220.

CALLOW, E. H. (1947): Comparative studies of meat I. *J. agric. Sci.*, 37, 113–127.

DAUMAS, G. & DHORNE, T. (1992): Problèmes statistiques posés par l'harmonisation des méthodes de classement des carcasses de porc dans la C.E.E. *J. Rech. Porcine en France*, 24, 47–54.

DIXON, W. J. & MASSEY, F. J. (1957): *Introduction to statistical analysis*. McGraw-Hill Book Co., New York, pp. 209–216.

ERDŐS, Z. (1998): *A minőségre ható rendszerek fejlesztése az élelmiszeriparban*. (Development of quality management systems in the food industry.) CSc Thesis. Hungarian Academy of Sciences, Budapest, pp. 57–66.

FÉNYES, T., ZUKÁL, E. & KÖRMENDY, L. (1970): Analitikai módszerek felülbírálatának és összehasonlító értékelésének matematikai problémái. (Mathematical problems in evaluating analytical methods.) *Kisérletügyi Közl., LXIII/E*, 41–47.

FULLER, W. A. (1987): *Measurement error models*. John Wiley & Sons, New York, pp. 2–5.

GÁBOR, E. (1983): Bestimmung des Eiweissgehaltes von Fleisch und Fleischwaren im ultravioletten Bereich. *Fleisch, 37*, 194–195.

GRAU, R. (1969): *Fleisch und Fleischwaren*. Paul Parey, Berlin, pp. 216–224 and 268–270.

HALD, A. (1964): *Statistical theory with engineering applications*. J. Wiley and Sons, New York, pp. 152–158 and 204–210.

HAMM, R., KÖRMENDY, L. & GANTNER, Gy. (1969): Transaminases of skeletal muscle 1. The activity of transaminases in post-mortem bovine and porcine muscle. *J. Fd Sci., 34*, 446–448.

HOFMANN, K. (1987): Neuere Tendenzen und Schwerpunkte in der analytischen Fleischforschung. *Fleischwirtsch., 67*, 1358–1364.

HORWITZ, W. (1982): Evaluation of analytical methods used for regulation of foods and drugs. *Anal. Chem., 54*, 784–806.

INTERNATIONAL STANDARD (1994): Accuracy (trueness and precision) of measurement methods and results, Part 1: general principles and definitions. ISO 5725–1.

KÁRPÁTI, GY. (1956): Beszámoló a KOHIKI Húsosztálya technológiai csoportjának 1955. évi működéséről. (Report on the activity of the Technological Department of the Research Institute for Canning, Meat Packing and Refrigeration in 1955.) *Húsipar, 5*, 35–40.

KÖRMENDY, L. (1958): Eljárás a páclevek nitrittartalmának gyors megállapítására.(Rapid method for determining the nitrite content of curing brines.) *A Konzerv-, Hús- és Hűtőipari Kutatóintézet Közleményei*, 1–2, 29–31.

KÖRMENDY, L. & ZUKÁL, E. (1992): Sur l'amélioration critique des méthodes analytiques. *Viandes et Produits Carnés, 13*, 103–107.

KÖRMENDY, L., GANTNER, Gy. & HAMM, R. (1965): Isosyme der Glutamat-Oxalacetat Transaminase im Skelettmuskel von Schwein und Rind. *Biochem. Z., 342*, 31–39.

KÖRMENDY, L., MIHÁLYI, V. & ZUKÁL, E. (1981): Az analitikai megbízhatóság megitélése.(On the reliability of analytical methods.) *Élelm. Ipar, 35*, 285–287.

KÖRMENDY, L., MIHÁLYI, V. & ZUKÁL, E. (1989): Comparison of analytical methods. *Meat Science, 26*, 193–207.

KÖRMENDY, L., ZSARNÓCZAY, G. & MIHÁLYI, V. (1992): A new, modified acid phosphatase assay for determining the extent of heat treatment in canned hams. *Fd Chem., 44*, 367–375.

LAWTON, W. H., SYLVESTRE, E. A. & YOUNG-FERRARO, B. J. (1979): Statistical comparison of multiple analytic procedures: application to clinical chemistry. *Technometrics, 21*, 397–404.

MANDEL, J. (1964): *The statistical analysis of experimental data*. Interscience Publishers, New York, pp. 369–389.

MIHÁLYI, V. (1973): Ist die Biuretmethode zur Schnellbestimmung des Eiweissgehaltes in Schinken brauchbar? *Fleischwirtsch., 53*, 705–706.

MIHÁLYI, V., KÖRMENDY, L. & RÉKASI, É. (1981): A Foss-let zsírmeghatározási eljárás értékelése. (Evaluation of the Foss-let method for determining fat content in meat and meat products.) *Húsipar*, *30*, 154–155.

MLYNARIK, J., SZARKA, E. & INCZE, K.(1964): Vizsgálatok a kenősáruk gyártástechnológiájának korszerűsítésére. (Modernization of the liver sausage processing.) *Húsipar*, *13*, 6–12.

NÁDAI, B. & MIHÁLYI, V. (1984): Investigation of different equations predicting moisture, fat and protein content of raw meat by NIR technique. *Acta Alimentaria*, *13*, 343–353.

NAGY, E., CZEGLÉDI-JANKÓ, J., ÉLIÁS, I. & KÖRMENDY, L. (2000): Rapid method for determining fat content in meat by using continuous wave nuclear magnetic resonance (CW-NMR) technique. *Acta Alimentaria*, *29*, 353–357.

NEMES, K. (1966): A szalámihúsok előkészítésének vizsgálata. (Study on the manufacture of salami.) *Húsipar*, *15*, 99–101.

OLSEN, E. V. (1997): Accuracy of industrial methods for quality measurements. *Proceedings of the 43rd International Congress of Meat Science and Technology*. Auckland, New-Zealand. *G2–22*, 678–679.

PIGGOTT, J. R. (Ed.) (1986): *Statistical procedures in food research*. Elsevier, London and New York, pp. 293–355.

PÜSCHEL, R. (1968): Zum Problem der Genauigkeit chemischer Analysen. *Microchim. Acta* (Wien), *4*, 783–801.

STEINER, E. H. (1967). Statistical methods in quality control. -in: HERSCHDOERFER, S. M. (Ed) *Quality control in the food industry*. Vol. 1. Academic Press, London and New York. pp. 121–216.

TIELMANN, J. (1991): Fettbestimmung von frischem Fleisch. *Fleischwirtsch., 71*, 643–644.

TOWNSEND, W. E. (1989): Stability of residual acid phosphatase activity in cured/canned picnic samples stored at –34 °C for 15 and 36 months. *J. Fd Sci., 54*, 752–753.

VENEGAS, O. & ANDÚJAR, G. (1979): Determination of chloride in meat products. *Proceedings of the 25th European Meeting of Meat Research Workers*. Budapest, Hungary. 5.12, 319–324.

WEBER, E. (1978): *Mathematische Grundlagen der Genetik*. VEB Gustav Fischer Verlag, Jena, p. 194.

WERNIMONT, G. T. (1987): *Use of statistics to develop and evaluate analytical methods*. Association of Official Analytical Chemists, Arlington, Virginia, USA, pp. 9–10.

YOUDEN, W. J. (1951): *Statistical methods for chemists*. J. Wiley and Sons, Inc. New York, pp. 40–41.

YOUDEN, W. J. & STEINER, E. H.(1975): *Statistical manual of the Association of Official Analytical Chemists*. Association of Official Analytical Chemists, Arlington, Virginia, pp. 21–27; 50–55.