KJELDAHL ANALYSIS

Advantages of automatised titration with pH measurement compared to automatised colorimetric detection

In chemistry the first method to detect if an aqueous solution was acidic or alkali was an indicator. It is a substance that changes colour depending on the pH of the solution. Since about 1940, the first pH electrodes were made giving the advantage of showing pH by a numerical value. Deriving the pH value from the colour change of an indicator was not necessary anymore. But the technology was initially expensive, and official methods did not take it explicitly into account as they were always written with the most simple standard laboratory glassware and chemicals allowing any basic lab to perform analysis according to official methods manually.

As automatization in laboratories increased, the first fully automatic steam distillation systems had an automatized colorimetric endpoint detection system. These systems needed very rigid parameters, as the automatic colorimetric detection has many limitations and deviances compared to the manual colorimetric detection with human eyes described in many old official norms.

C. Gerhardt introduced the first titration with pH measurement to detect end point for fully automatic Kjeldahl distillation units. The advantage is obvious especially in automation, as now, the system can handle directly numerical values. The detour via an indicator indicating that a certain pH endpoint is reached has been abolished. To comply with old official methods, it is always possible to set the end-pH with a pH titration system similar to the transition point of the referring indicator recommended in the old norm.

Modern official methods mention pH measurement as possible end-point detection or even recommend it to be better, especially with the C. Gerhardt technology "automatic endpoint" (see e.g. DIN/EN/ISO 5983-1:2005 Animal feeding stuffs – Determination of nitrogen content and calculation of crude protein content, point 8.3.3.1: "Titration with automatic endpoint indication using a pH-meter is recommended. Otherwise, the endpoint is indicated by the change in colour of the mixed indicator…".

Limitations of automatised colorimetric measurement:

- During manual titration with indicator as described in many old official methods, human eye detects brightness and frequency change of the indicator colour. This makes it possible to titrate manually with an indicator under light conditions where an automatized system would not be able to provide good results. All automatized colorimetric detection systems are therefore protected against outer light influences and need very stable and defined light in the titration cell to provide good results.

As the automatized colorimetric detection systems detect the endpoint by a certain intensity of a certain red and green colour frequency, all brightness influencing variables need to get fixed and the indicator solution precisely made, or the detection system would need regular adjustment to a certain brightness of the end-point red and green frequency. Any additional dilution of the boric acid indicator solution can lead to too low results because dilution raises the brightness of the colours which simulates that the end point has been reached.
There is one dilution parameter that cannot get fixed, it is the added titrant solution. An inter-laboratory comparison of one of the biggest lab chains in Europe has shown that especially in high protein samples, colorimetric detection can result in 0,2% to 0,35% lower protein results. One assumption is that high protein samples need a high addition of titrant which dilutes indicator solution, brightness rises and the system stops a bit earlier titration due to the higher brightness leading to lower titrant consumption and consequently, to slightly lower results.
These effects are not possible with pH measurement.

- For a reliable detection of the colour change of an indicator, the colour change must react very sensitively to pH change. This can be done by using a relatively weak boric acid concentration in receiver indicator solution. Furthermore, using only a small volume of the weak boric acid indicator solution. This will lead to quick colour changes as the pH changes rapidly. But there is one disadvantage that is compensated in old official norms by high boric acid concentration, usually 4% instead of 1% used in colorimetric systems. It is the risk of the boric acid receiver solution getting too alkali due to high protein content of sample. If the receiver solution becomes too alkali, ammonia will disappear as it cannot be trapped in an alkali receiver solution effectively. In automated systems, the solution to prevent this effect was to titrate always near to the colour change point even during distillation to prevent an alkali receiver solution. But it depends on the maximum speed of titration and the speed of ammonia coming over if the system works effectively. In colorimetric pH measurement, one cannot see if the boric acid solution reaches limits in alkali pH as the only indication is the change of colour in acidic receiver solution at one pH point. With pH measurement, all boric acid concentrations can be used, even 4% as described in many old methods. With a pH detection system, even the volume of boric acid can be chosen according preferences as it does not influence significantly accuracy of detection. Furthermore, a pH detection system can be set to parameters preventing safely alkali receiver solution because the system always knows at which pH the receiver solution is at present.
  Another assumption of the effect explained above of having lower protein results in high protein samples of automatic colorimetric detection systems is, that the colorimetric titration system cannot handle quickly enough the high amount ammonia coming over at high protein samples, due to weak boric acid concentration and low volume, the receiver becomes quickly alkali leading to slight ammonia losses.

To sum up, colorimetric automatized detection systems try to simulate under many limitations the manual colorimetric titration. The limitations make it necessary to even deviate in some points from some older official methods, for example by the boric acid concentration. The systems are more error prone as manual colorimetric titration, for example the influence of light coming from outside the system.

Automatic titration with pH measurement is state of the art technology, abolishing all disadvantages of automatic colorimetric measurement. Even all well-known titrator manufacturers promote pH measurement and offer colorimetric measurement only as a niche product.

The advantages of automatic titration with pH measurement have for years been recognized in international official methods (see e.g. DIN/EN/ISO 5983-1:2005 Animal feeding stuffs – Determination of nitrogen content and calculation of crude protein content; ISO 8968-1:2014 / IDF 20-1 Milk and milk products – Determination of nitrogen content – Kjeldahl principle and crude protein calculation; ISO 1971:2009 Food and feed products – General guidelines for the determination of nitrogen by the Kjeldahl method).

The flexibility and accuracy of automatized pH measurement titration meets or usually exceeds significantly the accuracy criteria specified for recovery and repeatability in old international methods describing manual colorimetric titration. In general, **C. Gerhardt guarantees, especially on the base of its pH titration technology that the systems will fulfil, as a minimum, the accuracy criteria specified for recovery and repeatability by all official national and international methods for Kjeldahl analysis.**