SOLVENT RESIN MANUFACTURERS

A sector group of cefic

FREE FORMALDEHYDE IN ALKYLATED AMINO RESINS BEST PRACTICE DOCUMENT

FINAL (21 March 2016)

This document is related to the Industry Standard DIN EN ISO 11402 4.3 Sulphite Method[1]. The purpose of this document is to describe best practise procedure according to the Industry Standard. The procedure itself as written in the Standard is the basis for this document.

USE OF DICHLOROMETHANE (DCM)

DO	DON'T
Use of DCM is mandatory for non-water soluble resins (if resin in water will not dissolve to a clear solution). In case of partly water soluble resins the use of DCM is recommended. Use pre-cooled (0 °C) DCM as written in the Standard to dilute resin sample before addition of ice-water and buffer solution.	Not recommended for water soluble resins.

STARCH – GRADES

DO	DON'T
The use of cold-water soluble Starch from Merck (1.01257.0050) prepared according to a modified procedure published by Zulkowsky is recommended. To avoid altering of starch solutions the direct use of powder starch is recommended as well.	Do not use too old starch solutions because detection of a clear end-point becomes difficult.

STARCH SOLUTION (PREPARATION, STORAGE TIME)

DO	DON'T
Direct use of cold-water soluble starch powder is recommended. No limitation of storage time.	Avoid: storage time > 2 weeks of aqueous starch solutions.

[1] This Best Practice Paper is related to the determination of free Formaldehyde in alkylated Amino Resins according DIN EN ISO 11402 4.3. For the determination of free Formaldehyde of un-alkylated Amino Resin (glues and impregnating resins) please refer to Formacare "Best practice for determining free formaldehyde in aminoplast resins": http://www.formacare.org/about-formaldehyde/health-safety/formaldehyde-air-monitoring/

SODIUM SULPHITE SOLUTION (PREPARATION, STORAGE TIME)

DO	DON'T
Dissolve 1 mol/l in cold demineralised water. Use solution within max 2 weeks (store at room temperature / in summer time in the fridge), not necessary to prepare fresh every day	Avoid: use of old sulphite solution

ICE (AMOUNT, SHAPE)

DO	DON'T
Use ice made from demineralized water. Use crushed ice. Use enough ice inside and outside.	Too low ice content during the whole time (most important!)

ADDITION OF RESIN SAMPLE

DO	DON'T
Stick to the recommended amount of resin sample in section 4.3.4.2 of the Industry Standard. During the first titration a measurable amount of Iodine has to be consumed, otherwise too much Resin Sample has been added and the results of the titration method are not valid (too low free formaldehyde will be reported).	Don't use too much resin!

ORDER OF ADDITION / PROCEDURE OF ADDITION (RESIN, ICE/WATER, DCM, BUFFER, AND TREATMENT)

DO	DON'T
Ad resin sample to beaker. For non-water (or low water soluble) resins add pre-cooled DCM and dissolve sample. Add ice water, crushed ice and pre-cooled buffer solution. Make sure that crushed ice is present in the mixture throughout the whole titration.	Avoid too low or too long time compared to procedure given in the Standard.

PRE-COOLING OF AGENTS

DO	DON'T
Use pre-cooled buffer solution and dichloromethane (DCM).	Don't use pre-cooled sodium carbonate due to tendency to crystallize.

MIXING (CONDITIONS)

DO	DON'T
Use efficient mixing device for homogenization of sample and added solutions (Ultraturax or efficient magnetic stirrer).	

Magnetic stirrer used by most of the companies

TITRATION TIME FINAL BACK TITRATION / DETECTION OF END-POINT

DO	DON'T
First titration completed in maximum 5 minutes after acetic acid addition. Waiting time for blue colour of 10 seconds is very important. Second titration after sodium carbonate addition to be completed in maximum 10 minutes. Waiting time for blue colour of 60 seconds is very important.	Deviate from waiting time for stable blue colour. Deviation may cause wrong results.

OTHER FACTORS

DO	DON'T
Make sure sufficient ice is present throughout the whole procedure. If required, add additional ice during titration. Adjust net weight of resin to expected free formaldehyde level.	Avoid solution to be above 0°C! Avoid too low ice content!

APPENDIX

Round-Robin Test Formaldehyde in Alkylated Amino Resins and Paints according to Industry Standard DIN EN ISO 11402 4.3 Sulphite Method

Author: Aschwin van der Horst (Nuplex)

Summary:

In this report the final results of the round-robin test for Cefic sector group SRM is reported. In this round-robin test the deviation for the determination method of residual formaldehyde determination in amino resins is determined by Industry Standard DIN EN ISO 11402 4.3 Sulphite Method and the conditions described in the Best Practise Paper above. The results are discussed and presented in the Cefic meetings. This report shows the overall conclusions of the round-robin test.

Conclusions:

- The absolute error for the determination of aqueous formaldehyde solutions by this method has been calculated to be 0.005%. This means, the titration method itself is very precise and all participating companies are able to determine formaldehyde concentrations of aqueous formaldehyde solutions with this method very precisely.
- From the obtained results in the round-robin test it can be concluded that it seems to be that the Industry Standard DIN EN ISO 11402 4.3 Sulphite Method is currently the best and most honest method to determine the free formaldehyde concentration of amino cross-linkers (alkylated amino formaldehyde resins). The relative Standard Error in the titration method is in between 0.6% and 2.9% of the measured average values for each individual sample measured by titration. The observed error is quite good for this kind of Round Robins.
- Each method based on chemical analysis may influence the equilibrium of bound and free formaldehyde. In the best practice document made by the melamine resin suppliers more details are given on the does and don'ts for this method. Important features in this document are e.g. Temperature of titration, indicator used, sample treatment and more.
- Overall it can be concluded that the DIN EN ISO 11402 4.3 Sulphite Method is the recommended method to determine the residual amount of formaldehyde present in alkylated amino resins with good significant results. Non chemistry based methods like NMR may not influence this equilibrium but are time-consuming and costly and not suitable for day-to-day analysis.

Introduction

The titration of formaldehyde in amino resins and paints is performed by several Alkylated Amino Resins producers. Three different samples were prepared and sent to the co-workers for analysis. The results for the round-robin test, calculation and determination of the standard deviations were determined according to the ISO-5725-2.

The method used is according to DIN EN ISO 11402 4.3 Sulphite Method. This is a titration method of a resin in dichloromethane/water suspension at 0ºC with iodine solution after addition of sodium sulphite. The titration method follows the reaction as given below:

- $CH_2O + Na_2SO_3$ (excess) + $H_2O \rightarrow HOCH_2\text{-}SO_3Na + NaOH$
- $ROCH_2OH + Na_2SO_3$ (excess) + $H_2O \rightarrow HOCH_2\text{-}SO_3Na + ROH + NaOH$
- >N-$CH_2OH + Na_2SO_3 \rightarrow$ No reaction at 0ºC
- excess $Na_2SO_3 + I_2 + H_2O \rightarrow Na_2SO_4 + 2\ HI$
- $HOCH_2\text{-}SO_3Na + I_2 \rightarrow$ No reaction at 0ºC
- $HOCH_2\text{-}SO_3Na + Na_2CO_3 \rightarrow CH_2O + Na_2SO_3 + NaHCO_3$
- $Na_2SO_3 + H_2O + I_2 \rightarrow Na_2SO_4 + 2\ HI$

In previous method evaluation there was concluded that the temperature of the titration is of most importance to avoid reaction of any “bounded” formaldehyde in the titration.

Samples

Three samples were prepared. The sample is called Alkylated Amino Resin:

- Alkylated Amino Resin, expected concentration is 0.46% residual formaldehyde
- Alkylated Amino Resin + formaldehyde, 80.66g of 37% formaldehyde in water added to sample Alkylated Amino Resin in a total amount of 2500g. Concentration calculated is 1.65% FFM
- Formaldehyde sample, a dilution of 3.3331g of 37% formaldehyde in water in 96.4417g of water. Concentration calculated is 1.28% FFM

Results

From the obtained results a z-score is calculated. The z-score is calculated from the "sigma" standard deviation of the individual measurements according to ISO-5725-2. The z-scores should be <=2.00 using average values in the round-robin test for every individual samples by every company participating in this round-robin test. The result of the Alkylated Amino Resin sample is given below: *Alkylated Amino Resin*

In Figure 1 the results of the z-score calculated according to the average values are depicted. In Figure 2 the results of the z-score calculated according to the real initial value is depicted.

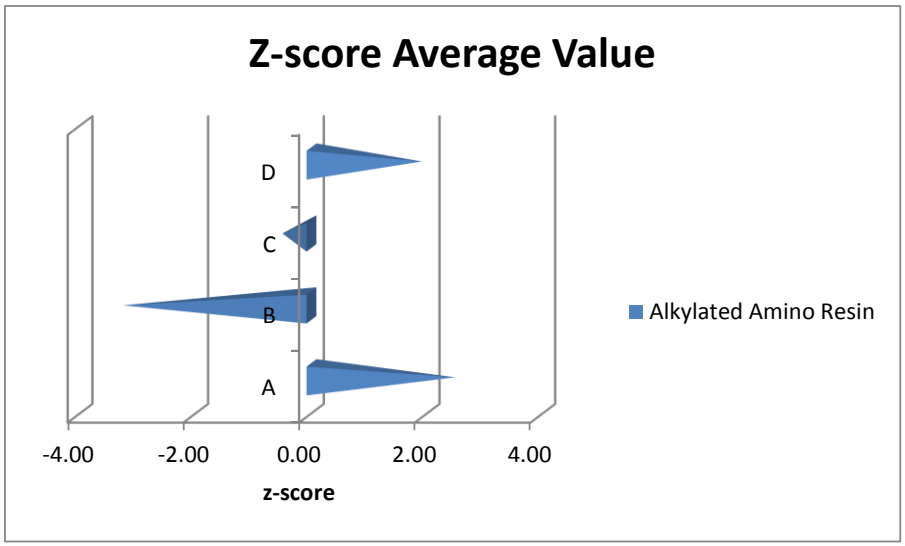

Figure 1 Z-score for Alkylated Amino Resin sample determined on average.

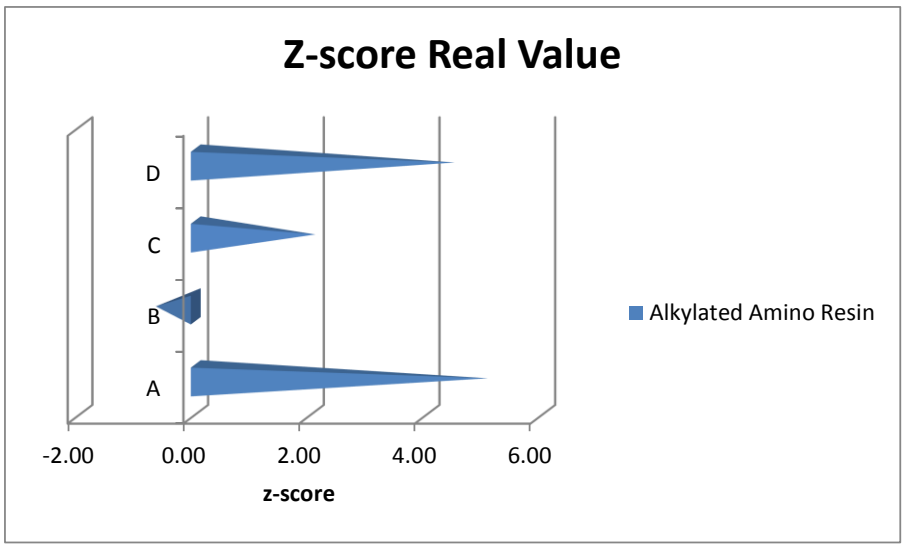

Figure 2 Z-score for Alkylated Amino Resin sample determined on real value.

The average value calculated for the so-called Alkylated Amino Resin is 0.50%. The reproducibility is 0.02% yielding a relative reproducibility of 2.9% on average. The range of tolerance is then 0.47% - 0.53% (|z-score| <=2.00). The F-test result yields a value of 25.7, $F_{3,7}$=3.63 indicating a good sample repeatability among individual measurements, but too high deviation in the sample results between the different participating laboratories.

Alkylated Amino Resin + formaldehyde

In Figure 3 the results of the z-score calculated according to the average values are depicted. In Figure 4 the results of the z-score calculated according to the real initial value is depicted.

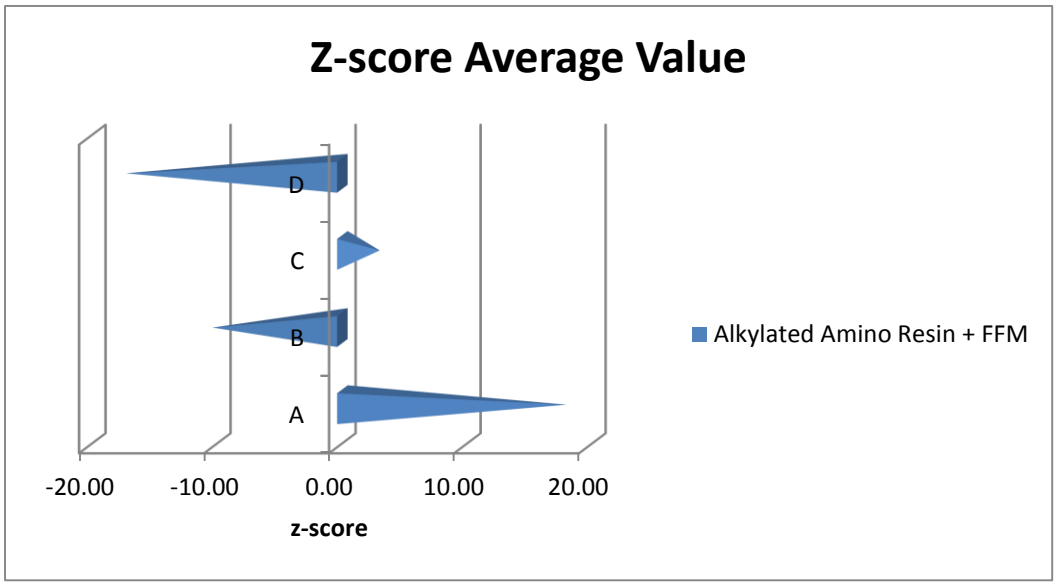

Figure 3 Z-score for Alkylated Amino Resin + formaldehyde sample determined on average.

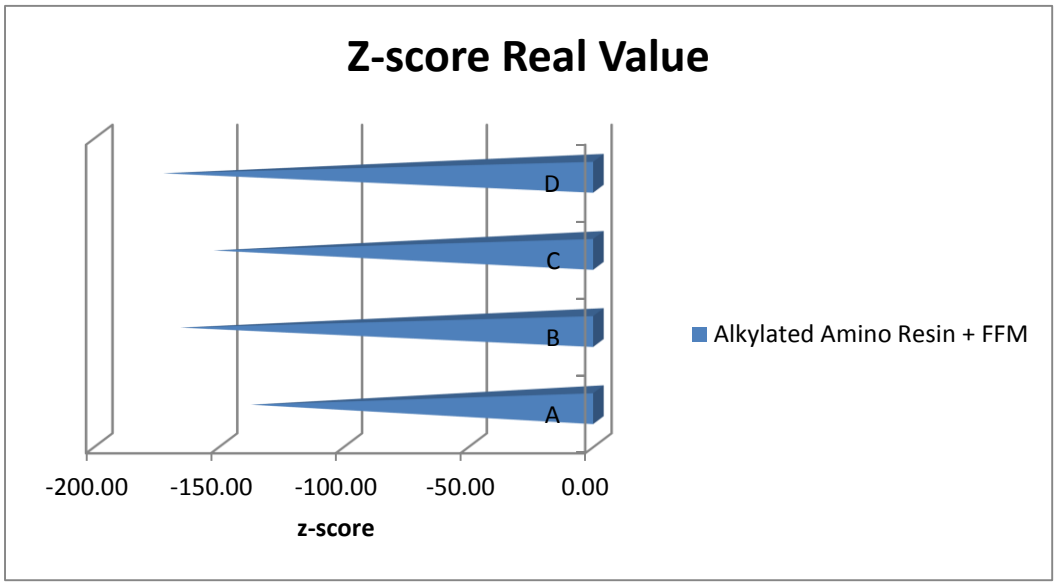

Figure 4 Z-score for Alkylated Amino Resin + formaldehyde sample determined on real value.

The average value calculated for the so-called Alkylated Amino Resin + additional formaldehyde is 0.82%. The reproducibility is 0.01% yielding a relative reproducibility of 0.6% on average. The range of tolerance is then 0.81% - 0.83% (|z-score| <=2.00). The F-test result yields a value of 0.86, $F_{3,7}$=4.35 indicating bad sample repeatability among individual measurements, but no deviation in sample results between the different participating laboratories.

Formaldehyde sample

In Figure 5 the results of the z-score calculated according to the average values are depicted. In Figure 6 the results of the z-score calculated according to the real initial value is depicted.

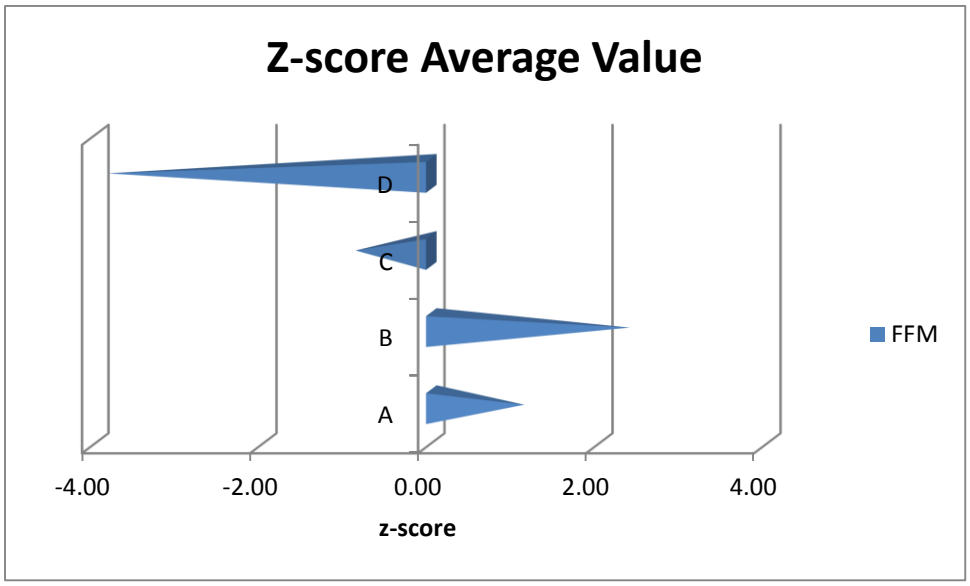

Figure 5 Z-score for the Formaldehyde sample determined on average.

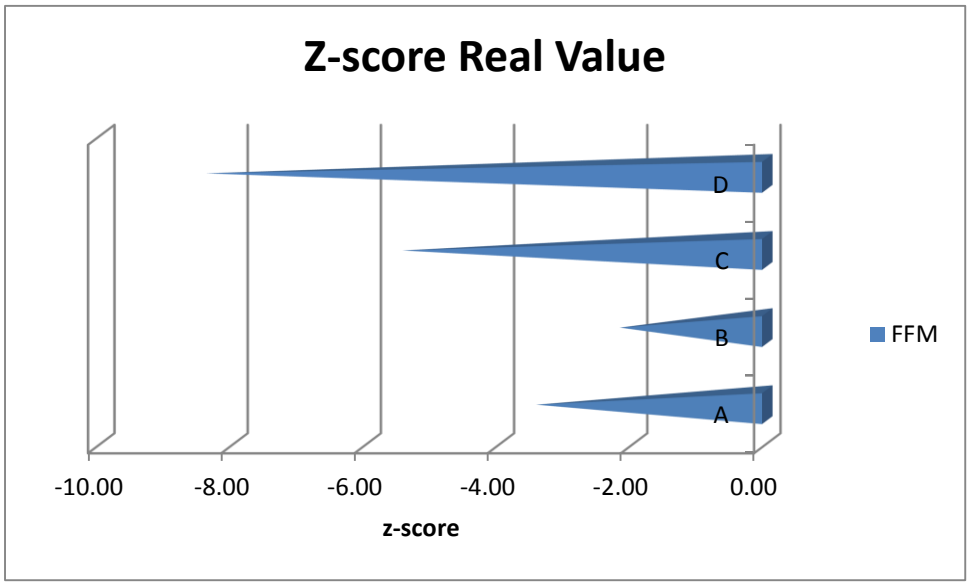

Figure 6 Z-score for the Formaldehyde sample determined on real value.

The average value calculated for the Formaldehyde is 1.16%. The reproducibility is 0.03% yielding a relative reproducibility of 2.9% on average. The range of tolerance is then 1.09% - 1.22% (|z-score| <=2.00). The F-test result yields a value of 110.3, $F_{3,7}$=4.35 indicating good sample repeatability among individual measurements, but too high deviation in sample between the different participating laboratories.

Conclusion

- The Relative Standard Error in the titration method is in between 0.6% and 2.9% of the measured average values for each individual sample measured by titration.
- When applying 0.1% tolerance for formaldehyde concentration in melamine resins and paints this method is suitable to determine the residual formaldehyde content in resins and paints according to the obtained reproducibility measured in this Round-Robin test.
- The Standard Error in the titration of 1.28% residual formaldehyde in water shows a standard deviation of 0.03% determined with an average of 1.16%. This was the best result because of a known concentration present in the water sample. The F-test results of this sample is 110.3, $F_{3,7}$=4.35 indicating good sample repeatability among individual measurements, but too high deviation in sample between the different participating laboratories.
- From the round-robin test it can be concluded that the addition of formaldehyde has influence on the determination method and therefore the error in the analysis. The deviation of the "real" value for this addition is the highest compared to the Alkylated Amino Resin and the Formaldehyde in water sample.

Additionally the individual companies determined the limit of detection of this titration method. The results are reported here as well.

Introduction

For the determination of the limits of determination, detection and quantification a calibration line was made of formaldehyde in water. Since the results of the individual measurements of formaldehyde in water by the companies (reported earlier in this report) participating in the round-robin test, it has been decided to use a formaldehyde solution in water to determine these limits. From a standard solution of 37% of formalin (formaldehyde in water) an aliquot of 3 grams was diluted in 100mL water yielding a concentration of about 1.11 % formaldehyde in water. From this stock solution the following calibration line was made (see table below).

Amount Stock:	Total Volume:	concentration:
1 mL	2 mL	0.56%
1 mL	5 mL	0.22%
1 mL	10 mL	0.11%
1 mL	25 mL	0.04%
1 mL	50 mL	0.02%
1 mL	100 mL	0.01%

The calibration-line was measured by titration according to Industry Standard DIN EN ISO 11402 4.3 Sulphite Method. The individually determined concentrations were plotted against known concentrations to determine the decision-limit (Lc), detection-limit (Ld) and determination-limit (Lq) according to Equation 1, 2 and 3.

Equation 1: Decision Limit

$$L_c = \frac{3\sigma_y}{B}$$

Equation 2: Detection Limit

$$L_d = \frac{6\sigma_y}{B}$$

Equation 3: Determination Limit

$$L_q = \frac{10\sigma_y}{B}$$

Where *B* is the slope of the calibration line and is called the sensitivity of the measuring method and can be calculated in Excel by the function *SLOPE*, σy is the precision of the measurement and can be calculated in Excel by the function *STEYX*. Figure 9, shows the explanation of the Lc and Ld in a calibration curve.

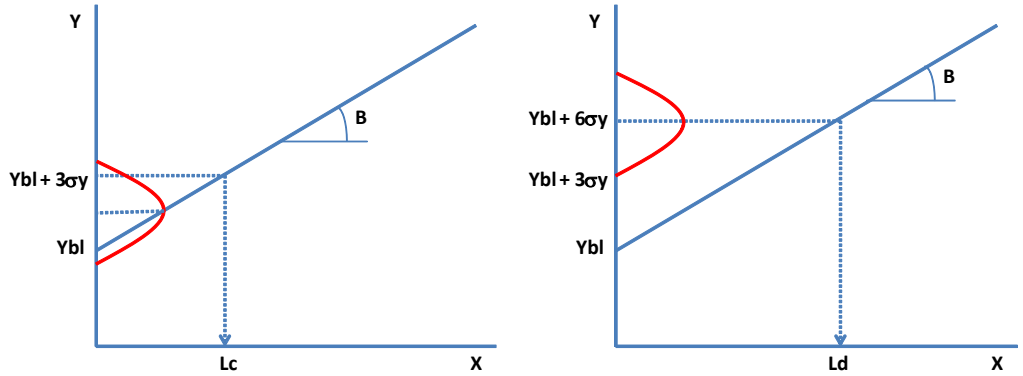

Figure 9: Explanation of the Decision Limit, Detection Limit.

The limits of decision, detection and determination are related to relative precision levels of 33%, 17% and 10%, respectively. When the sample concentration is further increased, the relative precision will be improved. However, in practice the relative standard deviation does not approach zero for high concentrations, but some constant value. At higher sample concentrations the random error of the signal often becomes proportional to the signal itself.

Results

After receiving the results of all participants the decision-limit (Lc), detection-limit (Ld) and determination-limit (Lq) was calculated for the pooled calibration results yielding the following results:

The limit of concentration, Lc has been calculated as 0.02%. That means, that if a value of less than 0.02% is obtained, formaldehyde should be reported as not detected.
The limit of detection, Ld has been calculated to be 0.03%. That means, if the value obtained is between 0.02% and < 0.03%, report free formaldehyde < 0.03%

The limit of quantification, Lq has been calculated to be 0.04%. That means, if the value obtained is lower than 0.04% but equal or higher than 0.03%, report as free formaldehyde < 0.04%, if the value is equal or above 0.04%, report the value obtained.

The absolute error for the determination of aqueous formaldehyde solutions by this method has been calculated to be 0.005%. This means, the titration method itself is very precise and all participating companies are able to determine formaldehyde concentrations of aqueous

formaldehyde solutions with this method very precisely. Nevertheless, the error reported from the previous discussed round-robin on amino resin samples of 0.6% and 2.9% as discussed in the results and conclusions of this report is not caused by the titration method itself but by the effect of the matrix of the amino samples.

Conclusion

- The absolute error for the determination of aqueous formaldehyde solutions by this method has been calculated to be 0.005%. This means, the titration method itself is very precise and all participating companies are able to determine formaldehyde concentrations of aqueous formaldehyde solutions with this method very precisely.

- From the obtained results in the round-robin test it can be concluded that it seems to be that the Industry Standard DIN EN ISO 11402 4.3 Sulphite Method is currently the best and most honest method to determine the free formaldehyde concentration of amino cross-linkers (alkylated amino formaldehyde resins). The relative Standard Error in the titration method is in between 0.6% and 2.9% of the measured average values for each individual sample measured by titration. The observed error is quite good for this kind of Round Robins.

- Each method based on chemical analysis may influence the equilibrium of bound and free formaldehyde. In the best practice document made by the melamine resin suppliers more details are given on the does and don’ts for this method. Important features in this document are e.g. Temperature of titration, indicator used, sample treatment and more.

- Overall it can be concluded that the DIN EN ISO 11402 4.3 Sulphite Method is the recommended method able to determine the residual amount of formaldehyde present in amino resins with good significant results. Non chemistry based methods like NMR may not influence this equilibrium but are time-consuming and costly and not suitable for day-to-day analysis.

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