Determination of formaldehyde in aminoaldehyde microcapsules

B. Boh[1], V. Ferk[1], E. Knez[2] B. Sumiga[1,2], M. Vrtacnik[1]
[1] University of Ljubljana, Slovenia (bojana.boh@ntf.uni-lj.si),
[2] Aero Chemical, Graphic and Paper Manufacturers, Celje, Slovenia (emil.knez@aero.si),

Introduction

Several analytical methods have been developed during the last decades for detecting, measuring and/or monitoring formaldehyde, its metabolites and other biomarkers of exposure to formaldehyde. Basic goals of these novel or improved analytical methods are primarily to lower the detection limits, and to enhance accuracy and precision of the methods. The most frequently used methods for the spectrophotometric determination of formaldehyde are based on reactions with chromotropic acid (1,8-dihydroxy naphthalene-3,6-disulphonic acid), acetylacetone (2,5-pentanedione) - NASH reagent, 3-methyl-2-benzothiazolone hydrazone - MBTH reagent, pararosaniline and sodium sulphite, malachite green–sulfite reaction (inhibitory effect of formaldehyde), and Purpald reagent (Aldrich Chemical Co.).

Materials and methods

Microencapsulation. Laboratory microencapsulation experiments were performed in a 2 L stainless steel reactor (diameter 180 mm) with Volrrath dissolver stirrer (diameter 80 mm) and regulation of with impeller speed 1200 to 6000 rpm, and a cooling/heating system. A modified *in situ* polymerisation method (Knez E., 1995; Kukovič M. and Knez E., 1997) was used as the basic microencapsulation process for the preparation of microcapsules with melamine-formaldehyde prepolymers as a wall material. Suspensions of prepared microcapsules were treated with a solution of Aluminium sulphate, microcapsules were precipitated, and formaldehyde was determinated in filtrates.

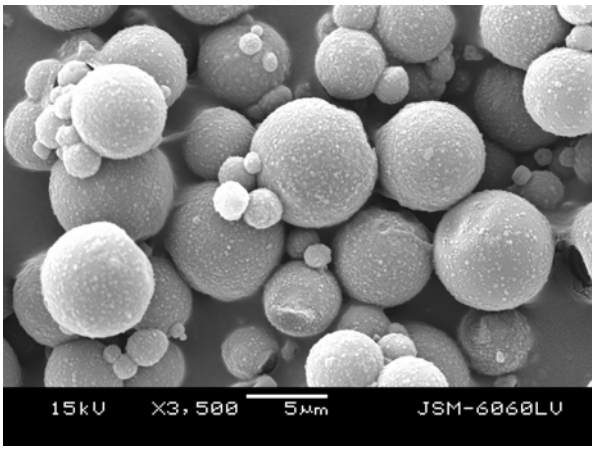
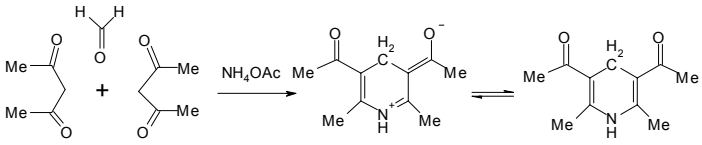


Fig. 1: SEM of microcapsules produced by *in situ* polymerization

Determination of formaldehyde. The **Edana 210.1-99 method** for formaldehyde determination is based on the first step of Hantzsch synthesis (Figure 2). This analytical method can be used for the quantitative determination of free formaldehyde and formaldehyde extracted partly through hydrolysis by means of water extraction.



Possible resonance structures of DDL

Fig. 2: Formation of the yellow coloured crystalline diacetyldihydrolutidine or diacetyldihydropyridine (DDL) during the first step of Hantzsch reaction

The **Malachite green method** has been developed for a colorimetric determination of very low concentrations of formaldehyde (Afkhami A. and Rezaei M., 1999). Malachite green chromatic form is a green dye. In the presence of sulphurous acid, a nucleophilic addition of HSO_3^- occurs, resulting in the formation of a colourless leuco form of malachite green, known as the Schiff's reagent (Figure 3).

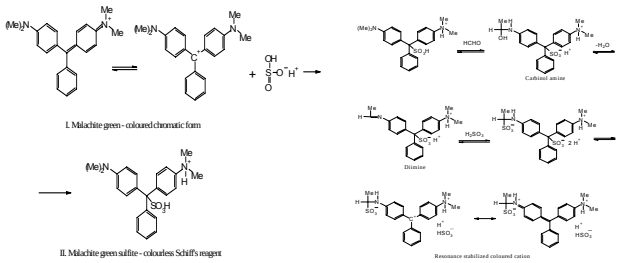


Fig. 3: Formation of colourless Schiff's reagent (left) and regeneration of the chromophore system of malanchite green (right)

Schiff's reagent reacts with aldehydes and through a series of reactions (first being nucleophilic addition of the Schiff's reagent to formaldehyde molecule) the chromophore system is regenerated via a carbinolamine, from which upon elimination of water a diimine is formed which further reacts with sulphurous acid to give rise to a resonance stabilized coloured cation (Figure 3). Ultra trace amounts of formaldehyde inhibit the malachite green–sulphite reaction in neutral media. This can be used for kinetic determination of ultra trace amounts of formaldehyde. The reaction can be monitored spectrophotometrically by measuring the decrease in absorbance of the solution at 613 nm.

Results and discussion

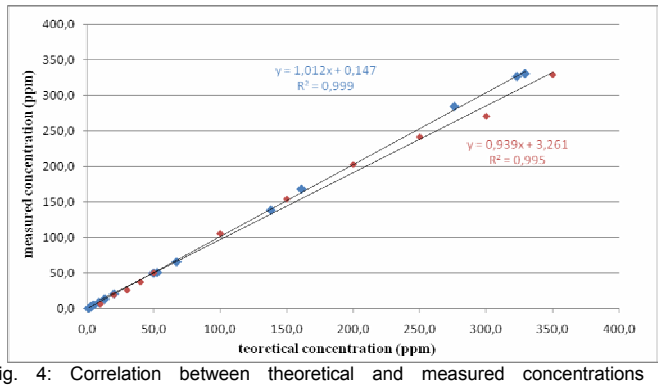


Fig. 4: Correlation between theoretical and measured concentrations of formaldehyde by Edana 210.1-99 method (blue) and Malachite green method (red)

Conclusions

Suspensions of microcapsules with melamine-formaldehyde polymer walls contain traces of residual formaldehyde as a result of the preparation method. Due to strict environmental standards, it is essential to keep the content of formaldehyde as low as possible, and to have reliable analytical methods for determination of low concentrations of formaldehyde. Our experiments have proven that Edana 210.1-99 method is appropriate for the determination of low (>10 ppm), and the Malachite green method of the ultra-low (>10 ppb) concentrations of formaldehyde in aminoaldehyde microcapsules and their formulations.

Acknowledgement

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References

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