Application Note 410000016-A

Quantification of Urea in Ethanol by Raman Spectroscopy

Urea in widely employed as a nitrogen-release fertilizer with more than 90% of urea production destined for agricultural applications[1]. Urea is also known to form complexes with fatty acids[2], which have been employed for separation of complex mixtures and purification processes[3]. In this application note, we present the quantification of the concentration of urea in ethanol by Raman Spectroscopy and show how this method can be employed for determining the percentage of urea in a solid inclusion compound with stearic acid[4].

Find more information in the video:

EXPERIMENTAL

Chemicals: Urea (Aldrich, >99%); Stearic acid (SA) (Aldrich, >95%); Ethanol (Soria)
Instrument: i-Raman® Plus 785S
Stock solutions of urea (0.0420 gr/gr ethanol) and SA (0.04126 gr/gr ethanol) were prepared. Standard solutions were prepared by mixing these stock solutions in different proportions in order to obtain urea concentrations between 0 and 0.042 gr/gr ethanol and keeping the total mass concentration (urea + SA) approximately constant. Raman spectra of 0.5 mL of each solution in aluminum containers were measured employing a 785 nm laser (power: 30%, ~ 90 mW) and 5000 msec of acquisition time (20 repetitions). No effects of heating or evaporation were observed. Spectra of the standard solutions that were background corrected employing the BWSpec® software are shown in Figure 1.

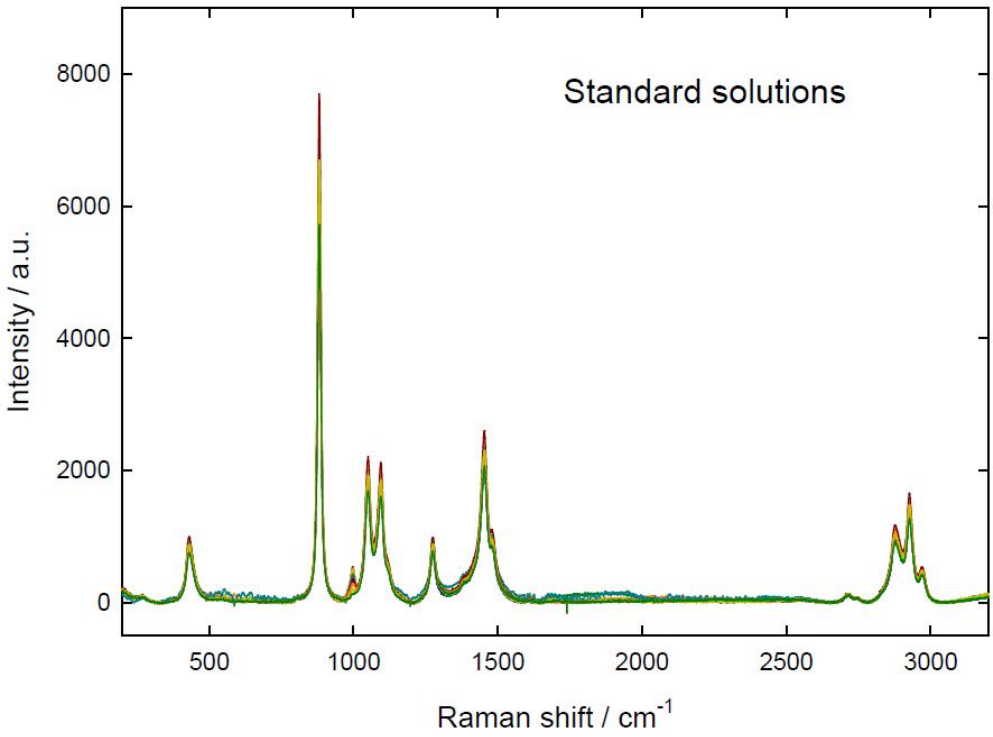

Figure 1. Dark-subtracted baseline-corrected Raman spectra of the standard solutions of urea and SA in ethanol.

RESULTS

Spectra were normalized by employing the intensity of the ethanol band at 1049-1050 cm^{-1}. Normalized spectra (Figure 2) clearly show that the only appreciable change due to the increment in relative urea concentration occurs at the band at 996-997 cm^{-1}, which is attributed to urea. This band corresponds to the symmetric C-N stretching[5] that is experimentally and theoretically reported at about 1010 cm^{-1} for the solid urea,[6] but shifts to lower wavenumbers in solution.[5,7]

For quantification purposes, spectra were deconvoluted, fitting the experimental results in the region 950-1200 cm^{-1} by 4 Lorentzian functions. These curve fitting results are shown in Figure 3 for some of the standard solutions.

The ratio of the intensities of the fitted peaks assigned to urea at 996 cm^{-1} (peak 1, a1) and ethanol at 1049 cm^{-1} (peak 2, a2) was employed as the analytical parameters. The dependence of this ratio on the urea concentration of the samples is presented in Figure 4. The calibration curve plotted in this figure shows a good linear behavior which indicates this parameter could be employed for urea quantification.

For the determination of the urea content of real samples containing both urea and SA, the solid sample was dissolved in ethanol (0.04299 gr/gr ethanol) and Raman spectra were recorded in the same conditions. From the values of the ratio a1/a2 for this sample, obtained by fitting of the peaks at 996 and 1049 cm^{-1} (Figure 5), the urea concentration of the solution was determined to be 0.03274 gr urea /gr ethanol. Thus, the urea content of the sample resulted to be 76 % w/w. This value is consistent with other reported values for the inclusion compounds formed by stearic acid and urea (ca. 75 %).[2,4]

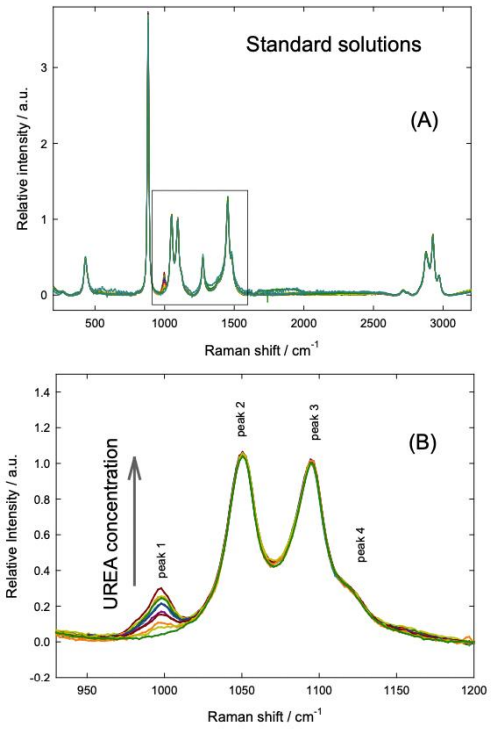

Fig.2: Normalized spectra of the standard solutions of urea + SA in ethanol. (A) Complete spectra (B) Analyzed region.

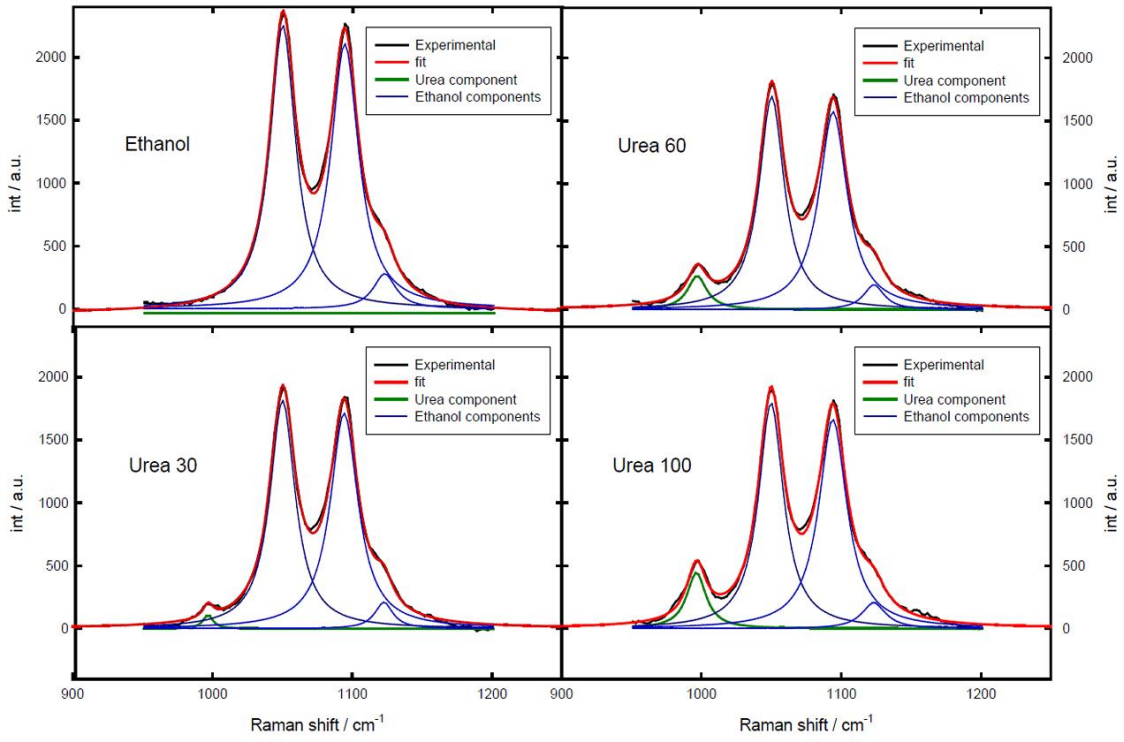

Figure 3. Fitting of the Raman spectra in the region 950-1200 cm-1. Urea 30, Urea 60 and Urea 100 mean solutions 0.0123, 0.0248 and 0.0413 gr urea/gr ethanol respectively.

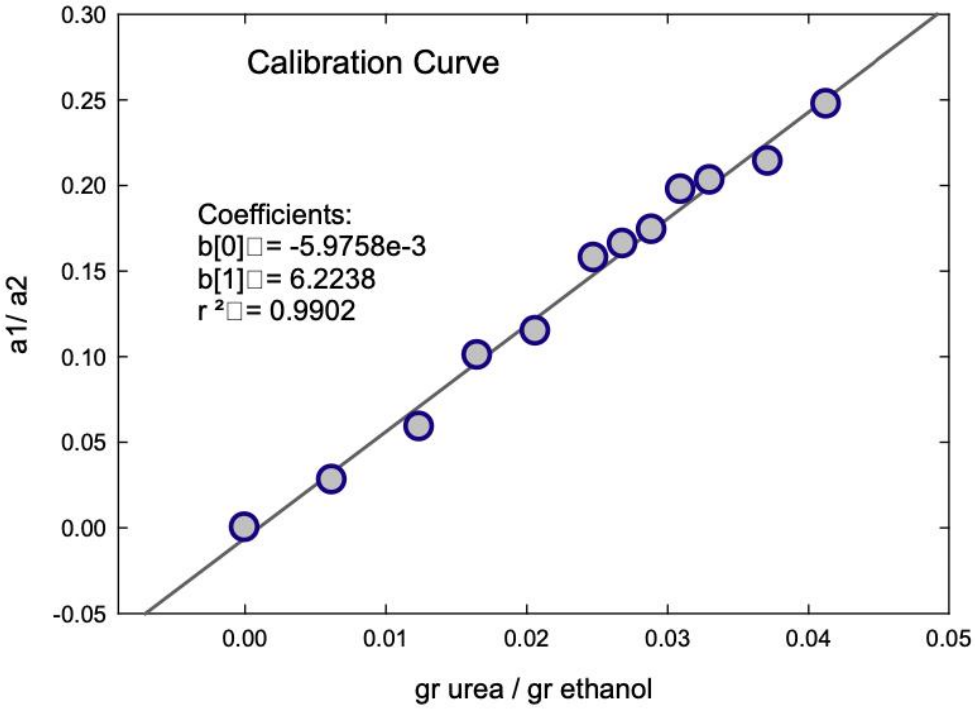

Figure 4. Calibration curve for the urea quantification in ethanol. Ratio of the intensities of the fitted bands of urea (a1) and ethanol (a2) as a function of the urea content of the standard solutions.

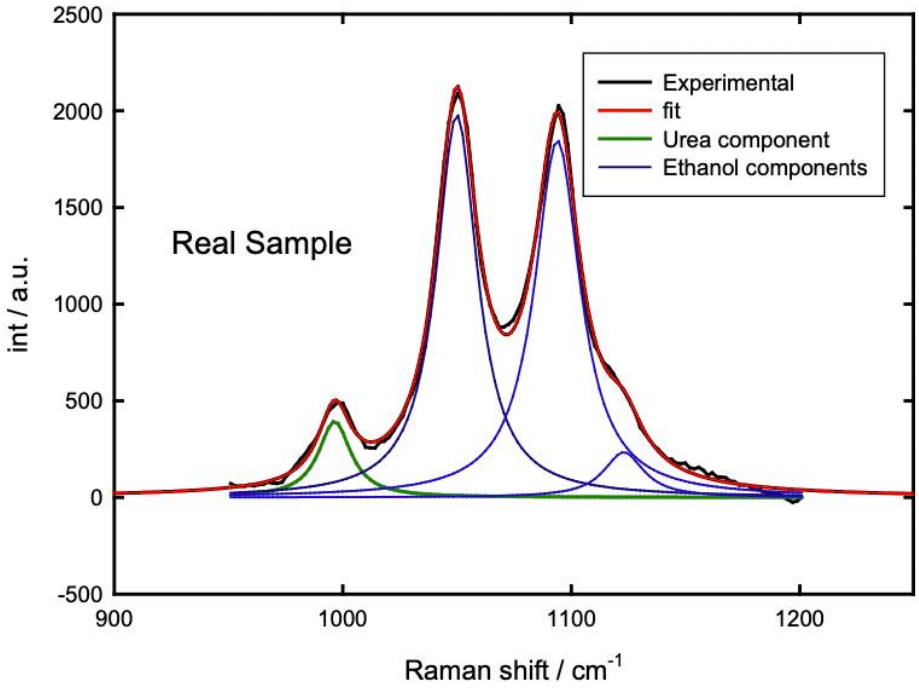

Figure 5. Fitting of the sample spectrum.

CONCLUSION

We presented a simple method for quantification of urea concentration in ethanolic solutions by Raman spectroscopy. The calibration curve presents good linearity in the concentration range analyzed (up to 0.042 gr urea / gr ethanol). The presence of stearic acid in the samples does not modify appreciably the Raman spectra (at least up to 0.042 gr / gr ethanol), so this method allows the quantification of urea in solid binary samples containing both urea and stearic acid.

FURTHER INFORMATION

Related application notes

Choosing the Most Suitable Laser Wavelength

Quantification of methanol in contaminated spirits with Raman

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CONFIGURATION

i-Raman Plus 785S Tragbares Raman-Spektrometer

Das i-Raman® Plus 785S ist Bestandteil unserer preisgekrönten Serie der i-Raman tragbaren Raman-Spektrometer mit unserer innovativen intelligenten Spektrometertechnologie. Dieses tragbare Raman-Spektrometer nutzt einen CCD-Array-Detektor mit hoher Quanteneffizienz, TE-Kühlung sowie hohem Dynamikbereich und liefert so eine hervorragende Leistung mit geringem Rauschen, selbst bei Integrationszeiten von bis zu 30 Minuten. Somit können auch schwache Raman-Signale gemessen werden.

Das i-Raman Plus 785S verfügt über die einzigartige Kombination aus einem breiten Spektralbereich und einer hohen Auflösung mit Konfigurationen, die Messungen von 65 cm^{-1} bis 3350 cm^{-1} ermöglichen. Die kleine Grundfläche des Systems, die leichte Bauweise und der geringe Energieverbrauch sorgen überall für die Möglichkeit, Raman-Analysen auf Forschungsniveau durchzuführen. Das i-Raman Plus ist mit einer faseroptischen Sonde zur leichten Probennahme ausgestattet und kann mit einem Küvettenhalter, einem Videomikroskop, einem XYZ-Verschiebetisch mit Sondenhalter sowie unserer unternehmenseigenen multivariaten Analysesoftware BWIQ® und der Identifikationssoftware BWID® verwendet werden. Mit dem i-Raman Plus haben Sie immer eine hochpräzise Raman-Lösung für qualitative und quantitative Analysen zur Hand.

Raman-Küvettenhalter für 9,5 mm Messsonde

Der BCR100A Raman-Küvettenhalter ermöglicht Ihnen eine einfache Messung des Raman-Spektrums von Flüssigkeiten und Pulvern durch Befestigung einer Raman-Sonde am Halter. Dieses Zubehörteil nutzt für unübertroffene Reproduzierbarkeit einen Innenspiegel mit einem Dreipunkt-Präzisionsverschluss und verstärkt das Raman-Signal dadurch bis zu dreimal mehr als herkömmliche Küvettenhalter. Er ist so konzipiert, dass der Sondenschaft die Küvette nicht direkt berührt, und umfasst eine Lichtfalle zur Verringerung der Hintergrundfluoreszenz. Der BCR100A ist in Modellausführungen für Sonden mit einem Durchmesser von 9,5 mm oder 12 mm erhältlich und kann zusammen mit jeder Standardküvette von 12,5 mm x 12,5 mm Aussendurchmesser (1 cm Weglänge) zur Probennahme bei Flüssigkeiten oder Pulvern verwendet werden.