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Direct nesslerization of ammonia and nitrate in fresh-water

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A method for measuring NH_3 colorimetrically by Nesslerization without distillation is proposed. Precipitation of $CaCO_3$ is prevented by adding Na salicylate, which chelates the Ca^{2+}, but not the Hg^{2+} of Nessler's reagent. NO_3^- can be measured in the same way after reduction with $TiCl_3$. Precision and accuracy are those of a colorimetric method ; the sensitivity is somewhat lower than with the indophenol-blue method using phenol, but about the same as when using salicylate.

Dosage de l'ammoniaque et des nitrates en eau douce par la méthode Nessler

Mots clés : Méthode, ammoniaque, nitrates.

Une méthode est proposée pour mesurer l'NH_3 par colorimétrie avec le réactif de Nessler, sans distillation. La précipitation du $CaCO_3$ est inhibée par l'addition de salicylate de soude, qui complexe le Ca^{2+}, mais pas le Hg^{2+} du réactif de Nessler. Le NO_3- peut être mesuré de la même façon, après réduction par $TiCl_3$.

La précision est semblable à celle des méthodes colorimétriques. La sensibilité est un peu plus faible que celle de la méthode au bleu d'indophénol utilisant le phénol, mais égale à celle qui utilise le salicylate.

Introduction

Nessler's reagent for ammonia has a high sensitivity and reproducibility, but a high blank as well. Interference is caused by Ca^{2+}, which precipitates as $CaCO_3$ at the high pH of the reagent. The first edition of the IBP handbook No 8 (Golterman & Clymo 1969) suggests that EDTA may be added to prevent the precipitate. As EDTA forms a complex with the Hg^{2+} from the reagent as well, the colorimetric reaction is no longer possible. In the second edition (Golterman et al. 1978) the method is omitted. As the idea of sequestering Ca^{2+} is correct, I looked for a complex that is sufficiently stable with Ca^{2+}, but not with Hg^{2+}. The chelating structure must lack N, so I looked for chelators with only oxygen in the active group. Salicylate appeared to have the necessary properties : when added at sufficiently high concentration, $CaCO_3$ does not precipitate, while salicylate has no influence on the colour of the ammonia-mercury complex.

Nitrate can be determined in the same way after reduction with $TiCl_3$ at high pH values (Minzoni et al. 1988). In this case, however, the $CaCO_3$ co-precipitates with the TiO_2 formed in the reaction, so the addition of Na-salicylate is no longer necessary. As the reducing agent contains a high concentration of NaOH, the Nessler's reagent is made up with less NaOH for the nitrate determination.

Methods

Ammonia

Nessler's reagent

N1 : Dissolve 25 g of HgI_2 (red) and 20 g of KI in 500 ml of H_2O.

N2 : Dissolve 100 g of NaOH in 500 ml of H_2O

N3 : Dissolve 50 g of NaOH in 500 ml of H_2.

IBP Nessler's reagent : Mix 1 vol. N1 + 1 vol. N2 and keep in a refrigerator. The mixed reagent is stable for at least 2 months.

IBP 1/2 Nessler's reagent : Mix 1 vol. N1 + 1 vol. N3 and keep in a refrigerator. The mixed reagent is stable for at least 2 months.

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Sodium salicylate solution (sol. « SS »)

Dissolve 10 g of Na-salicylate in H_2O and make up to 100 ml in a measuring cylinder. The solution is stable in a refrigerator for 15 days at least.

For the colorimetric determination of NH_3, mix 20 ml test solution, while shaking, with 1 or 2 ml of « SS » in a 25 ml volumetric flask followed, still swirling, by 1 ml IBP Nessler and make up to 25 ml. Measure the colour after 15-30 min at 420 nm.

Nitrate (+ nitrite)

Mix 45 ml of the test solution (or a smaller quantity made up to 45 ml) with 3 ml 10 M NaOH followed, still swirling, by 1 ml $TiCl_3$ in 15 % HCl (commercially available). Make up to 50 ml in a volumetric flask. After carefully mixing pour the black solution into a 50 ml reagent tube and leave covered till the precipitate is sufficiently settled so that a 10 ml sample can be taken, or centrifuge in a closed bottle. Put the sample into a volumetric flask of 25 ml, add 1 ml of Nessler's IBP 1/2 reagent, and make up with H_2O. Measure the colour as above for NH_3, NH_3 already present must be subtracted.

Results

First calibration curves were made using 20, 40, 60, 80 and 100 μg per 25 ml of H_2O. Typical results in a 1 cm cuvette were :

for NH_3 :

with Nessler IBP : all points :
$Y = 0{,}026 + 0.00795\ X \quad R^2 = 0.995$
all points minus the highest :
$Y = 0.014 + 0.00839\ X \quad R^2 = 0.999$
with Nessler IBP 1/2 : all points :
$Y = 0.034 + 0.00685\ X \quad R^2 = 0.998$
all points minus the highest
$Y = 0.030 + 0.0070\ X \quad R^2 = 0.998$

for NO_3 :

with Nessler IBP 1/2 : all points :
$Y = 0.046 + 0.00750\ X \quad R^2 = 0.993$
all points minus the highest
$Y = 0.031 + 0.00806\ X \quad R^2 = 0.9998$
where Y = abondance
and X = concentration (as N, in μg per 25 ml)

Nitrite should be measured separately and subtracted from the result in order to obtain the nitrate concentration.

Next calibration curves for NH_3 in H_2O and in Rhone water (Ca = 40 - 60 mg l^{-1}) were made. The slopes were O.00766 and 0.00755 respectively R^2 = 0.99 ; the standard errors of the estimate were about 0.0001 in both cases. In this case no differences were found it the highest points were deleted.

Discussion

The colour of the $NH_2Hg_2I_3$ complex depends on the NaOH concentration, up to the point where, after a while a precipitate forms ; there is no plateau. The extinction coefficients of the two Nessler's are, therefore, different and the colour after the nitrate reduction is different again. This means that calibration curves should be checked regularly. We measure the absorbance at 420 nm ; at lower wavelengths a higher absorbance will be obtained, but a lower ratio of signal to blank.

The IBP handbook records that the calibration curve is a straight line up to 100 μg of N-NH_3 per 20 m. With better curve fitting procedures than in 1969, I now believe that it is more precise to avoid concentrations > 90 μg per 25 ml, although the deviation from the straight line is small and was not found in all cases. A quadratic fit gave a slightly better result, but is not very practical.

The method is less sensitive than a colorimetric procedure applied after distillation, but more sensitive than a titration.

The sensitivity of the method falls in the range of values published for the indophenol-blue method of phenol (Verdouw et al. 1978) even after we improved the sensitivity of that procedure by a factor 2. The indophenol-blue method has further disadvantages, such as the use of phenol or similar products and a complex procedure.

The period needed to precipitate the TiO_2 after the nitrate reduction might be considered a disadvantage because of the possibility of NH_3 volatilization at the high pH of the reagent. I could not detect any loss under the given circumstances, however.

The Hg used can be simply precipitated as HgS and can be disposed of with an appropriate procedure. The quantity is small.

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