Determination of Nitrogen Losses in the Sulfuric Acid Solution, Waste of the $^{15}$N Separation Plant

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The most used method for production of stable isotope $^{15}$N is based on the isotopic exchange $^{15}$N/$^{14}$N in the nitrogen oxides-nitric acid solution system, known as Nitrox system. At the bottom of the packed separation column, the reflux is provided by total conversion of nitric acid into nitrogen oxides by reaction with sulfur dioxide, in a packed column type refluxer. The waste of $\text{HNO}_3-\text{SO}_2$ reaction is sulfuric acid, solution of 65-70%, which is evacuated at the bottom of the nitrogen oxides refluxer. The magnitude of the nitrogen losses, as $\text{NO}_x$ and/or $\text{HNO}_3$ in the waste sulfuric acid, were determined by analysing the effluent sulfuric acid by spectrofotometric method with Nessler reagent.

Keywords: isotope separation, Nessler reagent, sulfuric acid, nitrogen losses

At INCDTIM Cluj-Napoca, the stable isotope $^{15}$N is produced at concentration of 99 at. % $^{15}$N by isotopic exchange method $^{15}$N/$^{14}$N in (NO, $\text{NO}_2$)$_{(g)}$ – $\text{HNO}_3(s)$ system [1]:

\[
(\text{NO}, \text{NO}_2)_{(g)} + \text{H}^{14}\text{NO}_3(s) \leftrightarrow (\text{NO}, \text{NO}_2)_{(g)} + \text{H}^{15}\text{NO}_3(s)
\]

with a single stage separation factor: $\alpha = 1.055$, for 10M $\text{HNO}_3$, at 25°C and atmospheric pressure.

At the bottom of the packed separation column, nitric acid is total converted into nitrogen oxides by reaction with sulfur dioxide:

\[
2\text{HNO}_3 + 3\text{SO}_2 + 2\text{H}_2\text{O} = 2\text{NO} + 3\text{H}_2\text{SO}_4
\]

2$\text{HNO}_3 + \text{SO}_2 = 2\text{NO}_2 + \text{H}_2\text{SO}_4
\]

The nitrogen (enriched in $^{15}$N) losses in the waste sulfuric acid should be as much as few ppm of feeding nitric acid in order to have an efficient operation of $^{15}$N separation plant. The magnitude of nitrogen losses indicates the operating mode of the nitrogen oxides refluxer.

Colorimetric determination of ammoniacal nitrogen from different sources: rainwater [2], slaughterhouse [3], urine [4], blood [5] etc. can be done with Nessler reagent (potassium tetraiodomercurate II). This reagent is used for solutions that contain low ammonia concentration [6,7]. Ammonia forms with Nessler reagent an yellow complex [8]:

\[
2(\text{Hgl}_4)\text{K}_2 + \text{NH}_3 + 3\text{KOH} = \text{NH}_2\text{Hgl}_2\text{O} + 7\text{KI} + 2\text{H}_2\text{O}
\]

The colour intensity depends on the reagent composition [9].

Experimental part

For determination of nitrogen from waste sulfuric acid solution the calibration line was obtained by using sulfuric acid solution with known nitrogen concentration. That sample was placed in a modified Kjendahl apparatus, potassium hydroxide was added to neutralize the acid, then Dewar’s alloy, and the apparatus was heated in $\text{H}_2$ current for 15 min. The gaseous mixture containing ammonia, was bubbled in a flask with a known volume of 0.1 N $\text{H}_2\text{SO}_4$.

To that solution was added 1 mL of alkaline solution (10 g NaOH, 10 g Na$_2$CO$_3$ in 100 mL double distilled water) and 2 mL of Nessler reagent. Yellow colored compound immediately appeared and the absorbance of that sample was measured at 425 nm with UV-1800 Shimadzu spectrophotometer after 15 minutes. After plotting of the calibration line, the magnitude of nitrogen losses in the waste sulfuric acid have been determined.

The method requires a rigid control of the reaction conditions to prevent the turbidity of the solution [10].

Results and discussions

The calibration line (Fig.1) was obtained by using samples with known nitrogen content: 0.82 x 10$^{-6}$; 1.64 x 10$^{-6}$; 2.46 x 10$^{-6}$ and 3.28 x 10$^{-6}$ g N, obtained with 0.5; 1; 1.5 and 2 mL of NaNO$_3$ solution of 1.64 x10$^{-6}$ g N/mL.

The absorbance of the waste sulfuric acid samples was determined and the corresponding nitrogen concentrations were read from the calibration line.

Knowing that the $^{15}$N separation plant is fed with 60 moles of $\text{HNO}_3$/h, the nitrogen losses, calculated in ppm of the nitric acid flow, are presented (Table 1).

All waste sulfuric acid samples presented in Table 1 contain nitrogen (enriched in $^{15}$N) showing an improper operation mode of the refluxer.

\[
y = 0.094 + 0.0296x
\]

\[R^2 = 0.92686\]

Fig.1 Calibration line

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Conclusions

Any loss of nitrogen (enriched in $^{15}$N) is an additional, uncontrolled production that diminishes the normal production of $^{15}$N separation plant, indicating an improper operation of the nitrogen oxides refluxer.

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References

1. AXENTE D., ABRUDEAN M., BLDEA A., Separarea izotopilor $^{15}$N, $^{18}$O, $^{13}$B, $^{13}$C prin schimb isotopic, Casa Cartii de Stiinta, Cluj-Napoca, 1994, p. 125-146
2. NIEDZIESLKI P., KURZYCA I., SIEPAK J., „A new tool for inorganic nitrogen speciation study: Simultaneous determination of ammonium ion, nitrite and nitrate by ion chromatography with post-column ammonium derivatization by Nessler reagent and diode-array detection in rain water samples, Anal Chim Acta, 577, nr. 2, 2006, p. 220-224
3. LIN Y.M., LI L. Y., HU J.W., HUANG X.F., ZHOU C, JIA M., LI Z.B., Photometric Determination of Ammonia Nitrogen in Slaughterhouse Wastewaters with Nessler’s Reagent: Effect of Different Pretreatment Methods, Adv Mat Res, 955-959, 2014, p. 1241-1244
4. CONNERTY H.V., BRIGGS A.R., EATON E.H., Determination of Preformed Urinary Ammonia (Nitrogen) by Means of Direct Nesslerization, Am J Clin Pathol, 28, nr. 6, 1956, p. 634-638
5. MURAMATSU K., Direct colorimetric Method for the Determination of Free Ammonia in Blood, Agr. Biol. Chem., 31, nr. 3, 1967, p.301-308
6. JONG H., PARK J., KIM H., Determination of NH$_4$+ in Environmental Water with Interfering Substances Using the Modified Nessler Method, Journal of Chemistry Vol. 2013, Article ID 359217, 9 pages, http://dx.doi.org/10.1155/2013/359217
7. KRUG F.J., HANSEN E.H., RUZYCKA J., Determination of ammonia in low concentrations with Nessler’s reagent by flow injection analysis, Analyst, 104, nr. 1234, 1979, p.47-54
8. *** http://www.creeaza.com/referate/chimie/DETERMINAREA-AMONIACULUI-DIN_A812.php
9. GASTON Charlot, Les Methods de la Chimie Analitique, Masson et Cie, Editeurs, Paris, 1966, p.612-613
10. KOROLEFF Folke, Direct spectrophotometric determination of ammonia in precipitation, Tellus, XVIII, nr. 2, 1966, p.562-565

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\[
\begin{array}{|c|c|c|c|}
\hline
\text{Number of Sample (H$_2$SO$_4$)} & \text{Absorbance} & \text{Nitrogen losses x 10$^4$ (g)} & \text{Nitrogen losses (ppm)} \\
\hline
1 & 0.1370 & 1.510 & 5.78 \\
2 & 0.1505 & 2.125 & 7.28 \\
3 & 0.0943 & 0.018 & 0.06 \\
4 & 0.1825 & 3.328 & 11.88 \\
\hline
\end{array}
\]

Table 1

NITROGEN LOSSES IN SULFURIC ACID SAMPLES, WASTE OF $^{15}$N SEPARATION PLANT