

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

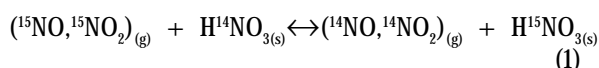
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The most used method for production of stable isotope ^{15}N is based on the isotopic exchange $^{15}\text{N}/^{14}\text{N}$ in the nitrogen oxides-nitric acid solution system, known as Nitrox system. At the bottom of the packed separation column, 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 HNO_3 - 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 NO_x and/or HNO_3 in the waste sulfuric acid, were determined by analysing the effluent sulfuric acid by spectrophotometric method with Nessler reagent.

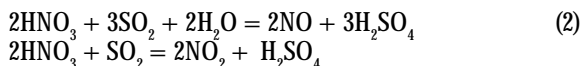
Keywords: isotope separation, Nessler reagent, sulfuric acid, nitrogen losses

At INCDTIM Cluj-Napoca, the stable isotope ^{15}N is produced at concentration of 99 at. % ^{15}N by isotopic exchange method $^{15}\text{N}/^{14}\text{N}$ in $(\text{NO}, \text{NO}_2)_{(\text{g})} - \text{HNO}_{3(\text{s})}$ system [1]:



with a single stage separation factor: $\alpha = 1.055$, for 10M 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:



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]:



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 Dewarda's alloy, and the apparatus was heated in H_2 current for 15 min. The gaseous mixture containing ammonia, was bubbled in a flask with a known volume of 0.1 N H_2SO_4 .

To that solution was added 1 mL of alkaline solution (10 g NaOH, 10 g Na_2CO_3 in 100 mL double distilled water) and 2 mL of Nessler reagent. The 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: 0.82×10^{-6} ; 1.64×10^{-6} ; 2.46×10^{-6} and 3.28×10^{-6} g N, obtained with 0.5; 1; 1.5 and 2 mL of NaNO_3 solution of 1.64×10^{-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 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.

$$y = 0.094 + 0.02659x$$

$$R^2 = 0.92686$$

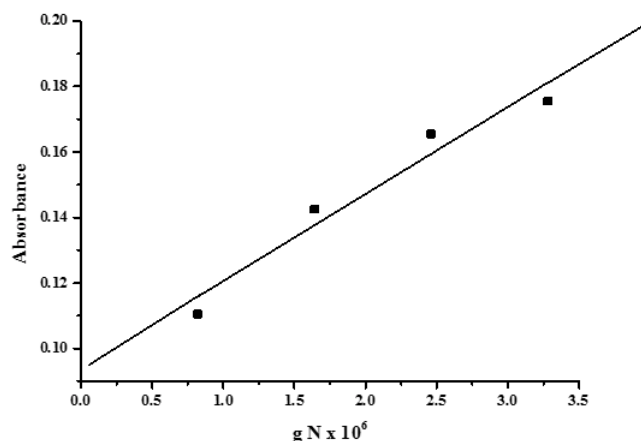


Fig.1 Calibration line

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Number of Sample (H ₂ SO ₄)	Absorbance	Nitrogen losses x 10 ⁶ (g)	Nitrogen losses (ppm)
1	0.1370	1.620	5.78
2	0.1505	2.125	7.58
3	0.0945	0.019	0.06
4	0.1825	3.328	11.88

Table 1
NITROGEN LOSSES IN SULFURIC ACID
SAMPLES, WASTE OF ¹⁵N SEPARATION
PLANT

Conclusions

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

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