The Collection Efficiency of $NH_3(g)$ in a Real Time Fluorometric Analyzer

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OBJECTIVES

GOALS OF THIS WORK:

- Calibration of a new sensitive instrument
- Determination of the instrument's detection limit
- Determination of the instrument's collection efficiency
- Permeation source testing

INTRODUCTION

WHY MEASURING AMMONIA?

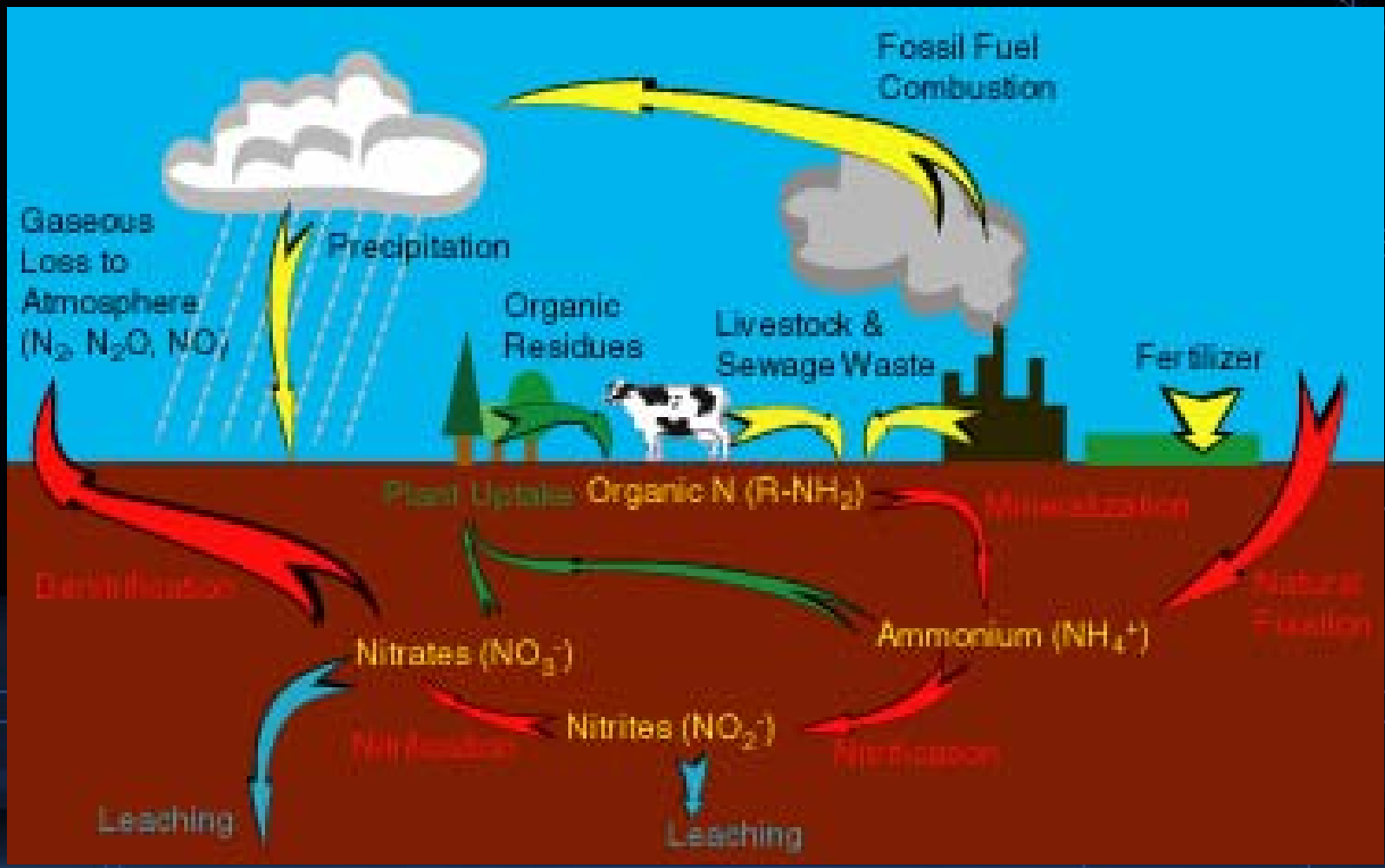
- **NH_3 is in equilibrium with NH_4^+ that is present in atmospheric aerosols [1].**
- **Aerosols affect climate cycles by changing the amount of sunlight that reflects back into space.**
- **The formation of aerosols induces the formation of clouds and decreases atmospheric visibility by light scattering.**
- **Breathing diseases caused by particle inhalation and accumulation in the human lung and other tissues[2].**

INTRODUCTION

- **NH_3 sources:**
  - **livestock waste**
  - **nitrogen fixation**
  - **chemical fertilizers**
  - **combustion and gaseous release from motor vehicles.**
- **All these factors induce an increase in NH_3 abundance which causes a change in the nitrogen cycle.**

INTRODUCTION

Fig.1 – THE NITROGEN CYCLE:



METHODS

TECHNIQUE FOR NH_3 MEASUREMENT:

- Fluorometric technique using a continuous flow method for NH_3/NH_4^+

- Voltage signals are collected using a computer data acquisition system, and are then plotted in the software for following analysis.

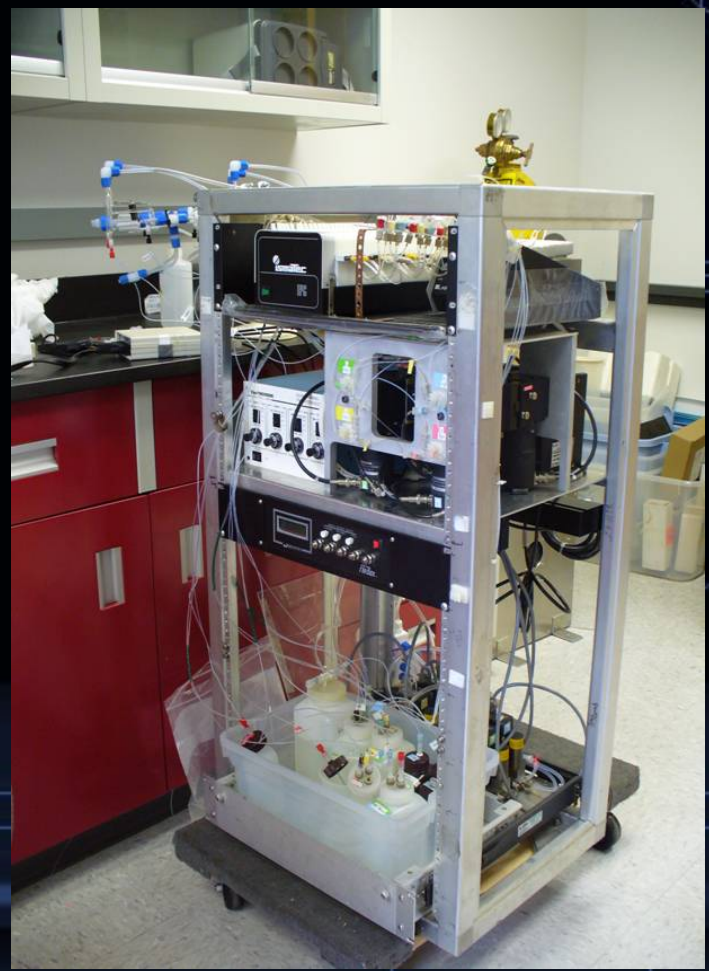


Fig.2 Picture of the NH_4^+ fluorometric analyzer.

METHODS

- Mixture of solutions by peristaltic pump and teflon tubing generate a product with fluorescence activity measured by a fluorometer.

- Aqueous solutions:
  - o-phthalaldehyde reagent
  - Borax/Sulfate pH9 buffer
  - pH6 buffer
  - NH_4^+ standard solutions

SCHEMATIC DIAGRAM

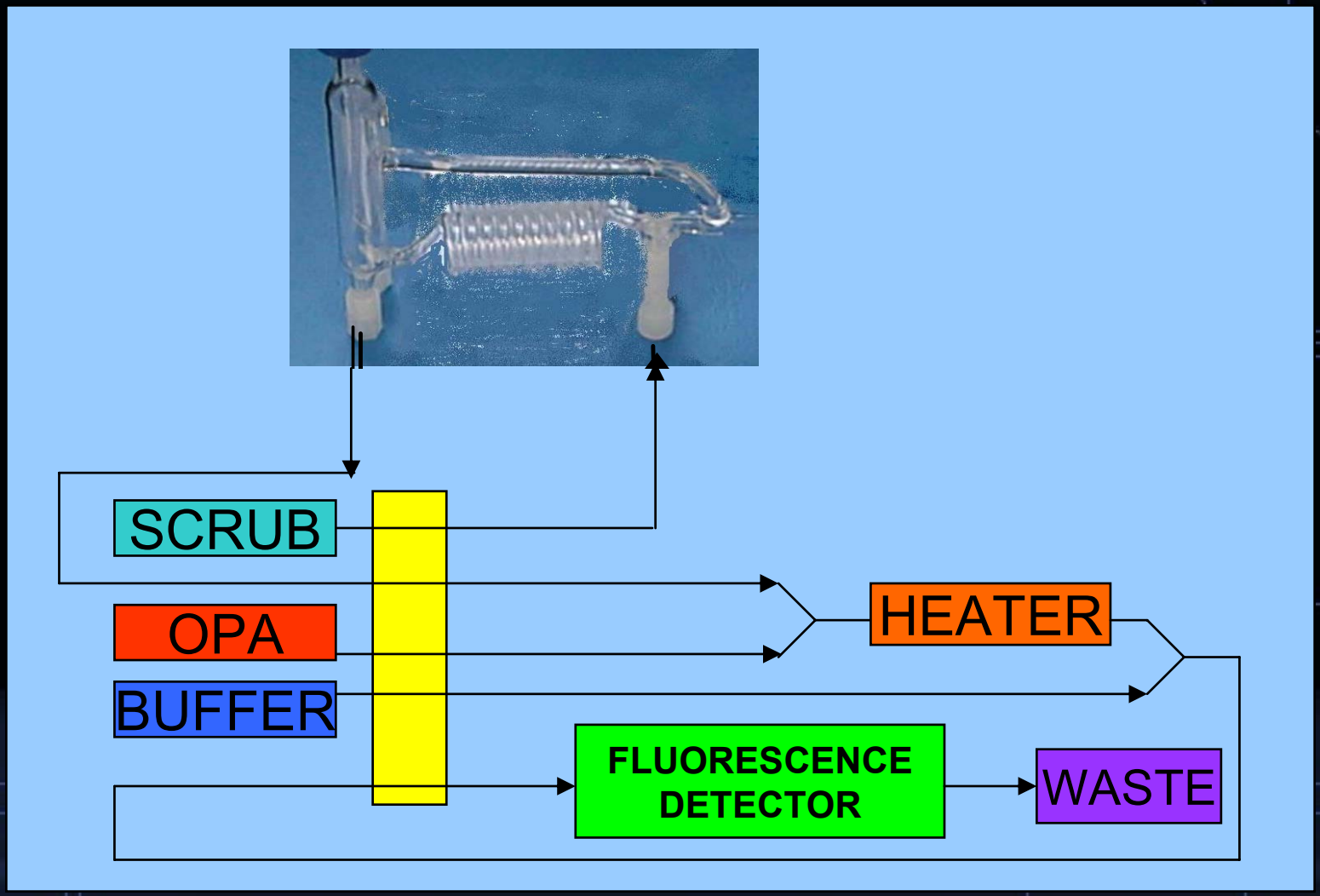


Fig. 3 Schematic Diagram of analyzer.

Fluorescence Spectroscopy Review

- Analytical technique involving electromagnetic spectroscopy based on atomic or molecular excitation –absorption of photons-

- When an electron absorbs a photon, goes to its excited state (π*); then collisions with other species cause a decrease in vibrational energy, then as it looses a photon it drops to its ground state again (π* → π or π* → n), generating fluorescence.

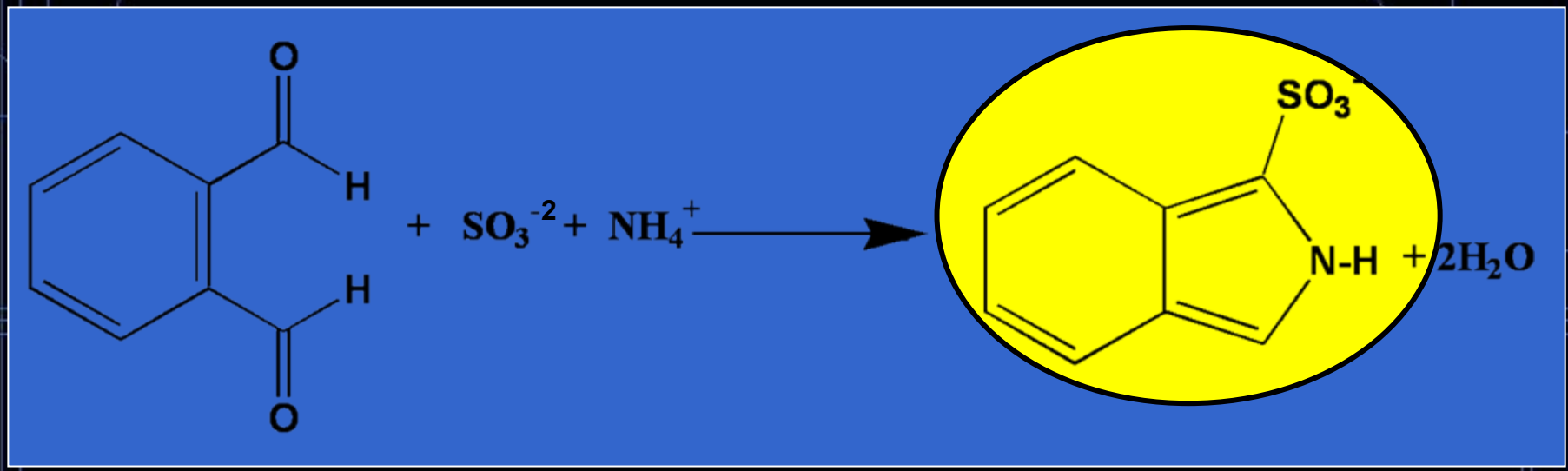
- Emissions are used to identify chemical species by qualitative or quantitative procedures

Fluorescence Spectroscopy Review

The following properties are some factors that increase **fluorescence** **[3]**:

(1) aromatic behavior -which exhibit lower energy transition levels-
(2) structural rigidity
(3) viscosity & low temperatures
(4) absence of heavy atoms
(5) resonance –gives stability, thus lower energy levels-
(6) lack of dissolved oxygen –reduces oxidation of species-
(7) low concentrations –decreases radiationless processes to occur-

CHEMICAL REACTION

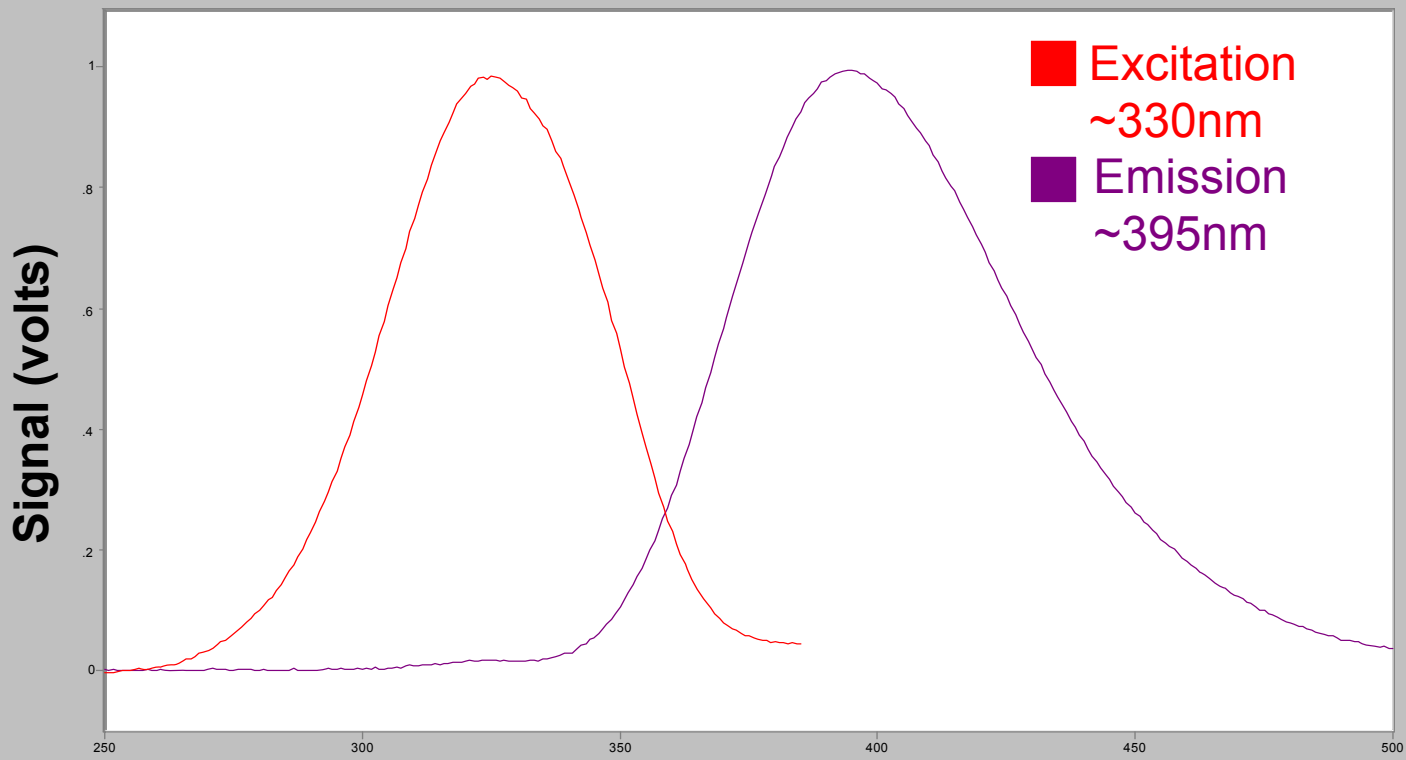


OPA
o-phthalaldehyde

isoindole

Fig. 4 – General reaction between primary alkylamines and OPA in prescence of an alkylthiol [4].

FLUORESCENCE SPECTRUM SCAN...



[Fig. 5]

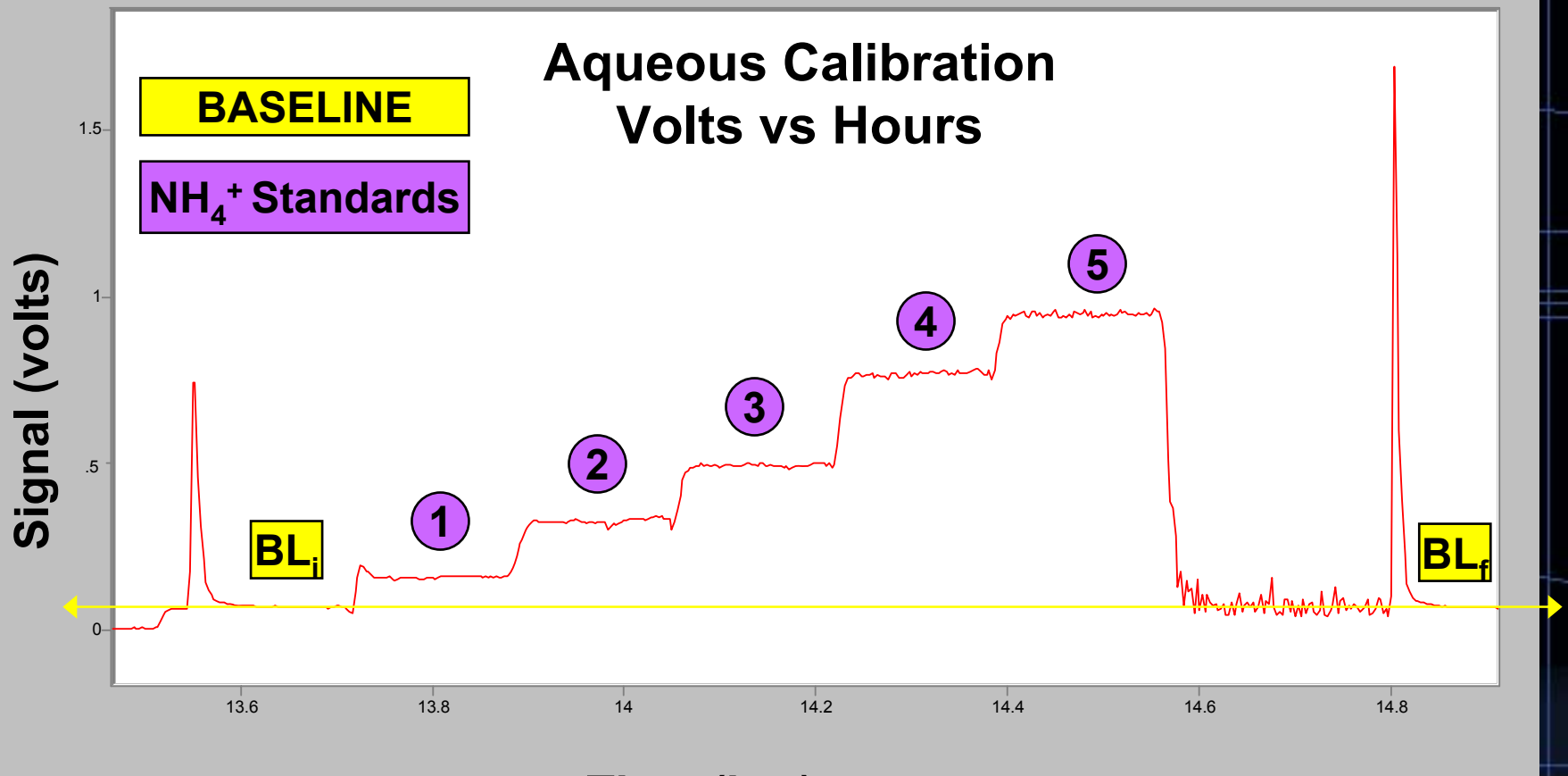
of progressive reaction

METHODS

AQUEOUS PHASE CALIBRATION:

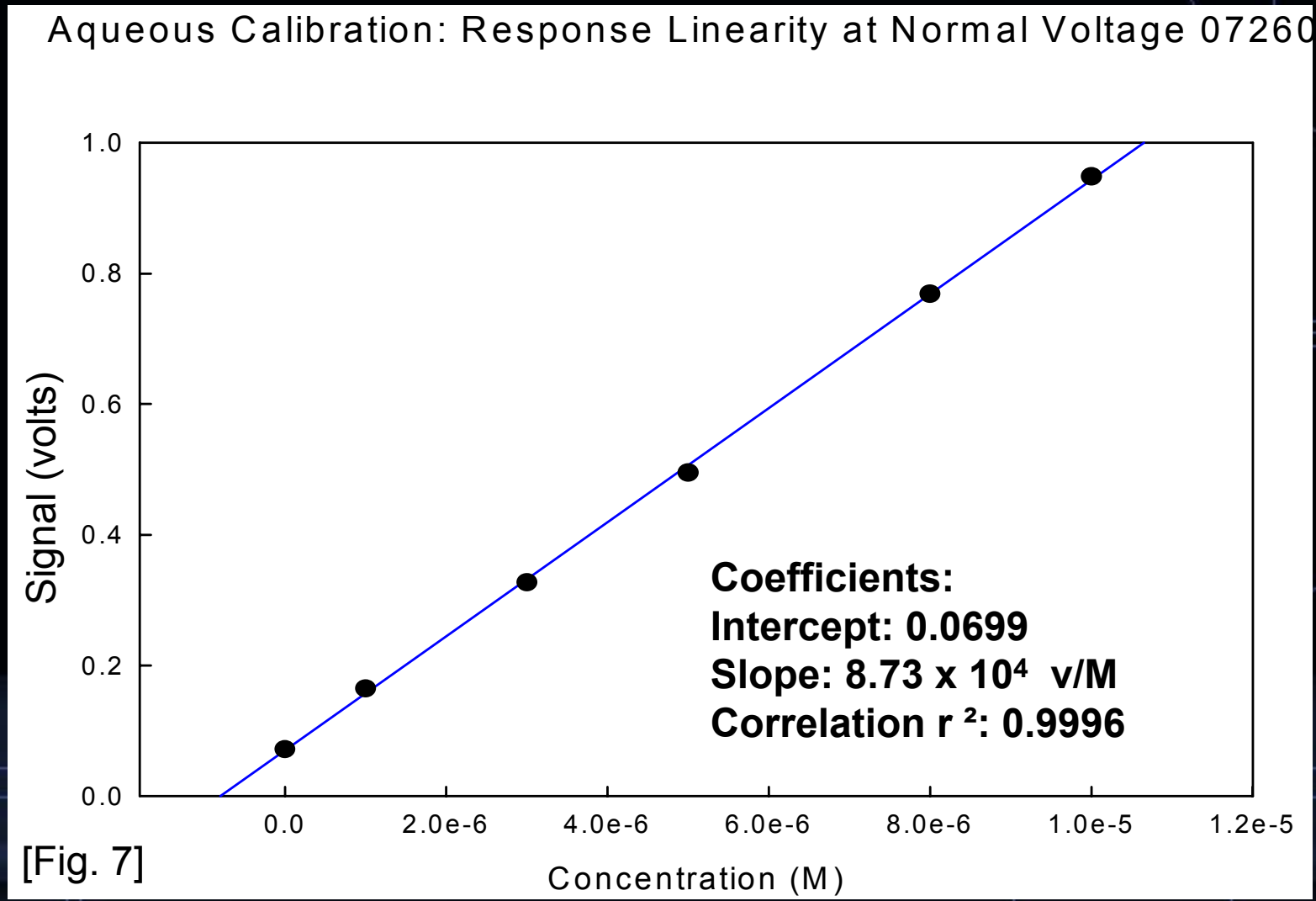
- The instrument runs with only the scrubbing solutions and the OPA and sulfite reagents for approximately 5 minutes to obtain a baseline.
- Afterwards, each standard solution is connected to the tubing in ascending order of concentration for 5 minutes per sample.
- This implies an ascending order of voltage, and the average voltage is next plotted against corresponding concentration. By analyzing the graphs and determining the slope, the detection limit can be established.

GRAPHS


Aqueous Calibration
Volts vs Hours
BASELINE
NH4+ Standards
Signal (volts)
1.5
1
.5
0
BLi
1
2
3
4
5
BLf
13.6
13.8
14
14.2
14.4
14.6
14.8
Time (hrs)
Arbitrary / Arbitrary
File # 2 = 072606
Paged Y-Zoom CURSOR
Res=None

[Fig. 6]

GRAPHS


Aqueous Calibration: Response Linearity at Normal Voltage 07260
Signal (volts)
1.0
0.8
0.6
0.4
0.2
0.0
0.0
2.0e-6
4.0e-6
6.0e-6
8.0e-6
1.0e-5
1.2e-5
Concentration (M)
Coefficients:
Intercept: 0.0699
Slope: 8.73 x 10⁴ v/M
Correlation r ²: 0.9996

[Fig. 7]

What is the detection limit?

- It is generally defined as three times the noise of the baseline.
- This gives us an idea of how low in scale can we trust the data obtained.

METHODS

GAS PHASE COLLECTION EFFICIENCY:

- $NH_3(g)$ permeation source is used
- Test the perm-source to confirm its flow rate of 100ng/min.
- We measured the response of our system to the known gas standard from the perm-source.

What is the collection efficiency?

- It is basically how much of the main reactive species we are actually recovering after being measured.
- This calculation proves how reliable is the procedure.

RESULTS & DISCUSSION

- Strong linear correlation was attained. The calibrations were done at two different concentration ranges.
- For concentrations from 0.1 x 10^{-5} M to 1.0 x 10^{-5} M, the correlation factor was r^2 = 0.9996, and it presented level noise of 0.00271.
- The calculated detection limit for this calibration was 9.3 x 10^{-8} M, which is equivalent to 0.68ppbv.
- Calibrations at high voltages are not reliable because a considerable increase in noise is seen after surpassing the 1.0 volts in the scale.
- The collection efficiency was calculated (PV = nRT) taking into account the dilution factor provided by the air flow rate and the expected NH_3 collection. The observed collection efficiency for NH_3 was about 20%.

FUTURE WORK

- Look for different ways of increasing the instrument's collection efficiency: different buffers, and/or air flow rates.
- Test its efficiency under field work conditions.
- Compare with other kind of instruments.
- Apply results to climate behavior and health effects.

REFERENCES

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- [2] McCubbin, D.R. et al. *Environmental Science & Technology.* Vol. 36, No. 6, 1141.
- [3] Skoog, DA; Leary, JJ. *Principles of Instrumental Analysis*, 4th Edition; Saunders College Publishing: US, 1992; pages 174-190.
- [4] Jacobs, W.A. *Journal of Chromatography*. 1987, 392, 435-441.

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