

Flow Injection Analysis of mineral nitrogen and phosphorus in soil

Past and Present

The Agricultural University in Poznań is one of several universities in Poland focusing on education and research in the areas of agriculture, forestry and animal husbandry. It was created in 1870 by August Cieszkowski, a prominent benefactor of science. After Poland gained her independence in 1919, it became the Agriculture and Forestry Department of Poznań University. The dynamic development of this department resulted in 1951 in the opening of an independent school named The August Cieszkowski Agricultural University (ACAU).

Today ACAU consists of the Faculties of: Agriculture, Forestry, Animal Husbandry, Wood Technology, Land Reclamation and Environmental Engineering. It has 10 000 - 11 000 students and lies at the forefront of research in agriculture, forestry, and food sciences. The Faculty of Agriculture – the largest – offers courses not only in agronomy but also in biotechnology, economics and environmental protection. It has several independent research units, one of them being the Department of Agricultural Chemistry (DAC), headed by Prof. Witold Grzebisz, who was instrumental in DAC's acquisition of a FOSS FIAsar™ 5000 flow injection analyzer in early 2004.

Scope of research

DAC is mainly involved in research on various crop requirements for nutrients. It also participates extensively in teaching and scientific investigation in the area of environmental protection. The following projects are currently running:

- Fertilization optimization of agricultural crops (recently focused on sugar beet, rapeseed/canola, winter wheat and malting barley)
- Forms and transformations of nutrients in soil
- Effect of sulphur on soils and crops
- Balancing of nutrients on the farm and in the natural environment
- Heavy metal transformations in soils and plants, their phytotoxicity and

means of alleviation/phytoremediation

- Determination of zones of ecological hazard

Nitrogen is the most important mineral nutrient for crops, determining their yield and quality. It occurs in soils in the form of organic (90-95%), and mineral (1-5%) compounds. Plants use mainly the mineral forms of nitrogen either as nitrates (N-NO_3) or as ammonium ions (N-NH_4). The content and mutual proportions of both nitrogen forms vary substantially from season to season, and depend on numerous factors (type of soil, pH, rainfall, temperature, crop rotation, etc). This is of importance for crops, since the mineral nitrogen content of soils determines the required rate of nitrogen application in the fertilization process.

On the other hand, determining optimum rate of nitrogen reduces the risk of contaminating the natural environment. Investigations into nitrogen balance in agriculture estimate the nitrogen utilization rate at 20%, based on the share of products sold from farms in relation to those bought from outside. This is attributed mainly to the low efficiency of feed nitrogen transformation by farm animals. The rate of nitrogen utilization in plant production is 60-80%. Nitrogen lost from both animal and plant production is dissipated in the environment through:

- (1) Leaching of nitrates to ground and surface water
- (2) Volatilization of ammonia into the atmosphere
- (3) Volatilization of denitrification products (NO , N_2O , N_2) into the atmosphere

One of the best-known consequences of contamination of the environment by agriculture is the increase in concentration of nitrate ions in surface and drinking water. Municipal waste accounts for the largest proportion of nitrogen dumped to surface water (approx 224 000 t/yr) – 55 per cent; then comes agriculture – 39 per cent.

There are two major sources of this contamination: natural fertilizers stored on farms (manure, dung), which cause

high point nitrogen concentrations over small surface areas, resulting in high risk of contamination; and fertilizers, both natural and mineral, applied to arable land in the course of agricultural production. The risk of nitrate loss from fertilizers after application is directly related to the climatic conditions in Poland. Generally, 20-30% of rainfall (500-600 mm) percolates either into deeper layers or runs off as surface water.

Phosphorus is the second strongest element after nitrogen, affecting plant yield and quality. As with nitrogen, excessive phosphorus in the environment accounts for many negative phenomena, for example eutrophication of surface and sea water. One of the highest concentrations of phosphorus in the environment was found in the Baltic and North Sea basins. About 13 000 t/yr of phosphorus from Polish territory is being discharged into Baltic waters, and agricultural production accounts for approx 50 per cent of this. So agriculture is the most important area of phosphorus control in the environment.

Method

These research projects need to be implemented using a suitable analytical method guaranteeing adequate accuracy and repeatability as well as high throughput, facilitating analysis of large sample populations. High throughput is of particular importance in the early spring, when immediate determination of rate of nitrogen is necessary due to intensity of farm work, rapidly changing growing conditions and plant growth stages. The accomplishment of defined production and assessment of leaching risk thus call for rapid and reliable analysis. Before DAC's acquisition of its FIAsar 5000 Flow Injection Analyzer, mineral nitrogen was analyzed mainly by the steam distillation method with MgO . Devarda's alloy was used for reduction of N-NO_3 . Distilled ammonia was trapped in 2-4% water solutions of boric acid, and later titrated in the presence of methyl red and bromocresol green indicators. The lower limit of determination depended on



soil/solution ratios and concentrations of titration acid. In theory at a 1:5 ratio, and for 0,0025 and 0,0010 M H₂SO₄, using a burette of 0,050 cm³ resolution, the calculated amount per resolution is 0,79 and 0,32 kg N/ha, respectively. Typical standard deviations are presented in Table 1.

Compared to the distillation method, the FIA results showed better repeatability and lower standard deviation (Table 1). However, the greatest advantages of the FIAStar 5000 were that less labour was involved and less chemical reagent was consumed. These greatly improve the economic aspects of soil analysis (Table 2).

Today mineral nitrogen (N-NO₃, N-NH₄) and phosphorus (P-PO₄) content are being determined by colorimetric method using the FIAStar 5000 from FOSS. Standard

chemical analysis consists of the following stages:

- (1) Collection of samples from various soil layers, e.g. 0 - 30, 31- 60 cm
- (2) Determination of moisture content and soil texture (we apply an organoleptic test for large sample loads)
- (3) Extraction of components (according to Houba et al. 1986: 0,010 M CaCl₂, soil:solution ratio 1:10, extraction time 2 h)
- (4) Filtration (filters from various manufacturers, filtrate must be clear)
- (5) Colorimetric analysis of N-NO₃, N-NH₄ and P-PO₄ by FIAStar 5000
- (6) Whenever necessary, determination of K, Mg and Na content in the same filtrate by ASA method.

The FIAStar 5000 Application Notes recommend the use of 2 M KCl solution for nitrogen extraction. For us, however, 0,010 M CaCl₂ proved to be much better, thanks to the possibility of simultaneous analysis of P, K, Mg and pH and the substantial reduction in use of reagents. We use a 40 µl injection loop for the determination of N-NH₄ and N-NO₃ (measuring range 0,1-5 mg/dm³). For P we often use a 400 µl injection loop, particularly when analyzing unfertilized soil (measuring range 0,005 - 1,0 mg/dm³).

Results

In the course of less than a year we have used our FIAStar 5000 to analyze approx

Cont. on page 22

Soil sample	Distillation method				FIAStar™ 5000			
	N-NH ₄		N-NO ₃		N-NH ₄		N-NO ₃	
	kg/ha	SD ^A	kg/ha	SD ^A	kg/ha	SD ^A	kg/ha	SD ^A
1	5,54	0,71	25,20	7,13	6,24	0,34	24,40	1,13
2	3,02	0,00	9,83	1,07	3,15	0,08	9,49	0,59
3	2,22	1,43	11,09	1,43	2,51	0,08	5,60	1,13
4	3,33	0,43	8,37	1,00	3,41	0,08	9,95	0,07
5	1,76	1,07	13,86	2,49	2,75	0,07	14,35	0,07
6	2,02	0,29	22,78	1,43	2,45	0,07	19,00	0,42
7	0,91	0,14	14,01	0,14	0,95	0,07	9,70	0,85
8	23,63	2,23	204,75	22,27	22,73	0,89	186,41	0,80
9	14,18	2,23	110,25	22,27	17,42	1,40	94,70	0,29
10	22,05	4,45	55,13	11,14	27,56	2,26	63,63	0,83
Mean	7,86	1,30	47,53	7,04	8,91	0,53	43,72	0,62

Table 1: Early spring mineral nitrogen (N_{min}) content of selected soil samples for two analytical methods (layer 0-30 cm).

^A – standard deviation for n = 2 (for FIAStar™ two samples randomly placed in the autosampler, and not two injections per sample).

Extracting solution– 0,010 M CaCl₂; soil:solution ratio 1:10. Correlation coefficients between the methods 0,971 and 0,991, for N-NH₄ and N-NO₃, respectively.

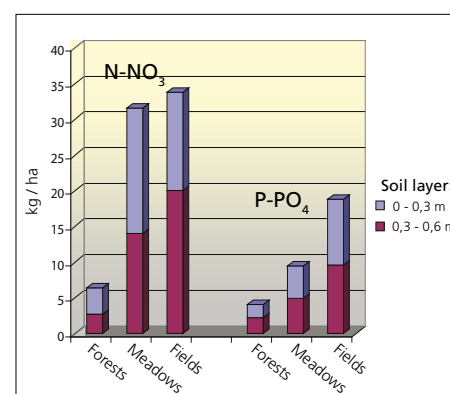


Figure 2: Nitrate and phosphate content of soil in various ecosystems. (Wyskocz river watershed near Poznań, May 2005).

Method	Form of nitrogen	Major cost producing reagents	Use of reagents ¹ (g/100 samples)	Cost of analysis of 100 samples ¹ (PLN)	Time of analysis of 100 samples ¹ (min)
Distillation	N-NH ₄	Magnesium oxide Boric acid Ethanol	20,0 20,0 5,0	38,40	500
	N-NO ₃	Devarda's alloy Boric acid Ethanol	10,0 20,0 5,0	42,40	500
	Totals	- - - -		80,80	1 000
FIAstar™ 5000	N-NH ₄	Indicator Sodium hydroxide Calcium chloride hydr.	0,021 1,033 3,189	3,35	107
	N-NO ₃	N-(1-Naphtyl) ethylene-diamine dichloride Sulfanilamide Ammonium chloride Calcium chloride hydr.	0,114 0,643 5,889 3,091	4,04 (18,04) ²	126
	Totals	- - - -		7,39	233 (260-270) ³

Table 2: Comparison of cost and time of analysis of mineral nitrogen content in soil for distillation and FIAstar™ 5000 methods.

¹ For FIA method only 1 injection per sample is calculated

² Including the cost of cadmium column replacement

³ Including time of method cassettes replacement and instrument calibration

14 600 soil samples, mainly for N-NO₃ and N-NO₄. During the early spring peak approx 4 500 samples were analyzed over approx 1,5 months (N-NH₄ and N-NO₃). Analysis results will be used in the preparation of fertilization recommendations and component balances of soil, plant, and selected farms. Since May 2004 we have also investigated the basins of two small rivers, situated in areas of high agricultural activity. Collected samples were analyzed for P-PO₄ as well as nitrogen. Preliminary results confirm the utmost significance of agricultural production in dissipation of these components in the environment. Typical N-NO₃ and P-PO₄ contents of soil of various utilization patterns are presented in Figure 1.

Our FIAstar 5000 has also occasionally been used for analysis of nitrogen content in plant as well as lake and river water samples. We have investigated inter alia the effect of fertilization on the quality of potatoes (N-NO₃ content in fresh tubers), and overall nutrition of sugar beet plants (N-NO₃ content in petioles of fifth to seventh leaves). In both cases nitrates were analyzed in a 2% solution of acetic acid.

Conclusions

One analytical module of the FIAstar 5000 is currently in use. It requires frequent changes of method cassette depending on the ion being analyzed. Nevertheless the rate of soil analysis, repeatability of results and reduced use of chemical reagents indisputably favour the FIAstar compared with our former methods. Using the instrument facilitated execution of a much greater number of analyses than before. It also extended the scope of our research, particularly in the area of environmental protection. The purchase of our next FIAstar 5000 module is planned for the future. It would further improve the throughput of analyses and also let us add further analytical parameters, primarily boron.

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Dr Barłóg operating the FIAstar™ 5000.