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Development of a Gas Dialysis System for $\text{NH}_4\text{-N}$ Determination

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Abstract

The development of a gas dialysis system proved that ammonium-N recovery was inversely proportion to acceptor flow rate. The relationship between ammonia trapping and acceptor flow rate was considered a crucial parameter and the best flow rate for donor and acceptor streams was chosen for the analysis of water and extract samples. The Technicon silicon gas dialysis membrane showed very low ammonia transference. Polytetrafluoroethylene (PTFE) membranes allowed higher amounts of ammonia to be transferred through them. Recovery of ammonia using the standard 6 inch dialyser was 56.7 percent. Analysis at 20 samples per hour showed adequate peak separation and good peak shapes. The standard deviation of the results was between 0.002 and 0.004 for a 1 mg l^{-1} ammonium-N solution. Calibration curves were linear ($y = 4.14 + 15.7x$, $r^2 = 0.99$ and $y = 5.11 + 42.82x$, $r^2 = 0.98$). Hence, the developed system was sufficiently precise and reliable for its use in $\text{NH}_4\text{-N}$ determination.

Introduction

Chemical interferences caused by certain organic nitrogen compounds in the ammonium-N determination by the automated Berthelot reaction urged the need to include a gas dialysis system with the Technicon AutoAnalyzer II as a pre-treatment step to eliminate these interferences. Distillation or gas phase dialysis can separate ammonium-N from interferences caused by organic nitrogen compounds. Crowther and Evans (1980) included the distillation as a pre-treatment step in ammonium analysis and obtained 95 percent recoveries of added ammonia from solutions of 55 test compounds. They run the samples at rate of 20 per hour and noted that the calibration for the system was linear. Recent research has focused on the inclusion of the gas dialysis using a PTFE gas permeable membrane as pretreatment in the FIA systems. Van der Linden (1983) has tested several microporous hydrophobic membranes for the determination of ammonia in fresh water systems. Martin and Meyerhoff (1986) described a method for using a PTFE membrane in a home made dialysis with wider channels instead of commercially available dialysis in a flow injection system. They reported that nitrogen dioxide is transferred across a teflon membrane in the dialysis and converted to nitrate by a buffered peroxide recipient solution. They concluded that a dialyser with wider channels improves the efficiency of gas transfer and thus the detection capabilities of the system. Willason and Johnson (1986) described a procedure based on the conversion of ammonium-N in sea water to ammonia and the subsequent diffusion of ammonia across a hydrophobic membrane using flow injection dialysis.

There is criticism on ammonium-N determination by routine methods as Schulze *et al.* (1988) criticised Nesslerization and the Berthelot reaction for determining sub micromolar levels of ammonium in sea-waters, certain surface waters, glacial and glacial ice. They proposed that gas separation is satisfactory. Some parameters are of crucial importance for the selection of membranes, analyte concentration etc. For instance, Van Staden and Rensburg (1990) evaluated the commercially available semi-permeable

membranes for use with parallel-plate dialysis in flow injection system. They reported that the fraction of analyte transferred from the donor to the acceptor stream depends on the type of membrane used, membrane surface, membrane line-length, membrane porosity, concentration of analyte in the donor stream, the use of concurrent and counter current flow between the donor and acceptor streams and flow rates of the donor and acceptor streams. These characteristics of PTFE gas dialysis may affect the performance of the continuous flow analysis method, for example if included with the Technicon AutoAnalyzer II system of ammonium-N determination. Therefore, it seemed appropriate to select the optimal conditions to develop a dialysis system which could be included with $\text{NH}_4\text{-N}$ system manifold of the Technicon AutoAnalyzer II.

Materials and Methods

Studies were carried out in the Department of AFE, University of Glasgow for the development of a dialysis system and its inclusion with the Technicon AutoAnalyzer II to eliminate the interferences caused by the organic nitrogen compounds in the determination of $\text{NH}_4\text{-N}$. The glassware used in these studies was first washed with hot water and soaked overnight in a 2 per cent solution of Decon 90 (Decon Laboratories limited). These were then washed with hot water, rinsed twice with deionized water and finally dried in an oven at 70°C .

Ammonium nitrogen was measured by a modification of the indophenol green method using a complexing reagent to prevent interferences due to the precipitation of hydroxides in the reagent system. With the inclusion of a sodium nitroprusside catalyst, the sensitivity of the method was such that ammonium could be determined in the range of 0 to 1 ppm and with care 0 to 0.1 ppm (Brown, 1973). This method is applicable to water samples and a wide range of soil extractant solutions, acid digests of plant or soil material. The schematic diagram of the original flow system is shown in Fig. 1. The dialysis system was included with AutoAnalyzer II main manifold for determining $\text{NH}_4\text{-N}$ as shown in Fig. 2.

1M NaOH: Forty gram sodium hydroxide was dissolved in 500 ml of deionized water in 1 litre volumetric flask. After cooling, the volume was made upto the mark with deionized water.

2M HCl: One hundred and seventy ml concentrated HCl was diluted with deionized water and volume was made upto the mark in 1 litre volumetric flask.

1M HCl: Eighty five ml concentrated HCl was diluted with deionized water in 1 litre volumetric flask upto the mark.

0.01M HCl: Ten ml of 1M HCl acid were pippered into 1 litre volumetric flask and volume was made upto the mark with deionized water.

Gas Dialysis System: Technicon silicon rubber membrane (product No. 157-13129) of the Technicon Corporation, New York, USA was used in the dialysis system. Dialysis system included with $\text{NH}_4\text{-N}$ main manifold of Technicon AutoAnalyzer II comprised of dialysis block (6" dialyzer of the Technicon Corporation, New York, USA).

Gas Dialysis membranes

Tetrafluoroethene (TFE) 1" x 600: This was a product (Part No. 14-831-3006) of Fisher Scientific Co; USA.

Polytetrafluoroethene (PTFE) 1" x 600: This was a product (Military Specification) of Gortex W.L. and Associates, Inc; Newyark, Delaware, USA.

Dialysis blocks: These were 3" and 6" dialyzers of the Technicon Corporation, Newyork, USA.

Results and Discussion

The changes made in the original dialysis system shown in the Fig. 1 resulted in the system shown in the Fig. 2. The main objective of the experiments was to find out the best flow rates of air, acid, sodium hydroxide and sample through the donor and acceptor streams of the dialysis system.

Air elimination from the acceptor side of the dialysis improved the flow. The flow stabilized and the peak shape improved. However, the ammonium recovery was low. Therefore, the optimization of the flow rates through acceptor and donor sides of the dialysis was carried out using balanced and unbalanced flows.

Some of the possible combinations of the following flow rates of the different parameters were tested using the system 2 shown in the Fig. 3 and the results are shown in Table 1.

Air flow = 0.32, 0.60 and 0.80 ml/minute.
Sample flow = 0.23 and 0.42 ml/minute.
NaoH (1M) flow = 0.10 and 0.16 ml/minute.
HCl (0.01M) flow = 0.23, 0.42, 0.60 and 0.80 ml/minute.

The number of air bubbles and their surface area might have impact on the percentage recovery of ammonia through the

membrane. The effect of air flow rates is evident from the Table 2.

Table 1: Effect of flow rate on ammonium-N measurement.

Air Flow (ml)	Sample Flow (ml)	NaOH Flow (ml)	NaOH Conc. (M)	Total Donor (ml)	Acceptor Flow (ml)	Peak Height
0.60	0.23	0.10	1M	0.93	0.32	23.0
0.80	0.23	0.10	1M	1.13	0.32	23.5
0.32	0.23	0.10	1M	0.65	0.32	26.5
0.32	0.32	0.10	1M	0.74	0.42	11.5
0.80	0.32	0.10	1M	1.22	0.42	13.0
0.32	0.42	0.16	1M	0.90	0.60	3.5
0.80	0.42	0.16	1M	1.38	0.60	4.0
0.32	0.23	0.10	1M	0.65	0.60	3.5
0.32	0.32	0.16	1M	0.80	0.80	1.0
0.32	0.42	0.16	1M	0.90	0.42	9.0
0.32	0.42	0.16	1M	0.90	0.32	24.0
0.32	0.42	0.16	1M	0.90	0.23	51.5
0.32	0.23	0.10	1M	0.65	0.42	13.5
0.32	0.23	0.10	1M	0.65	0.32	24.0
0.32	0.23	0.10	1M	0.65	0.23	39.5
0.32	0.42	0.16	1M	0.90	0.23	50.5

Table 2: Effect of air flow at various acceptor flow rates on ammonium measurement.

Air flow rate (ml/minute)	Acceptor flow rate (ml/minute)		
	0.32	0.42	0.60
0.32	26.5*	13.0	4.0
0.60	23.0	-	-
0.80	23.5	11.5	3.5

*Peak heights

There is small increase in ammonium recovery as air was reduced but is not equivalent to the change in the donor system residential time. So, air flow rate is not an important parameter affecting the recovery of ammonium-N.

It was assumed that the sample flow rate may affect the ammonium recovery. Some data was selected from the Table 1 and presented in Table 3 to show the relationship between the donor and the acceptor flow rates. The first ammonium concentration of the donor solution (sample plus sodium hydroxide) was equal in the donor stream but the residential time was different. It is clear from the peak heights that faster flow resulted in the greater transfer of ammonia through the membrane, only at low acceptor flow rate.

Table 3: Effect of two donor flow rates at various acceptor flow rates on ammonium measurement.

Donor flow rates (ml/minute)	Acceptor flow rates (ml/minute)			
	0.23	0.32	0.42	0.60
0.65	39.5*	24	13.5	3.5
0.90	50.5	24	9.0	3.5

*Peak heights

The acceptor flow rate was inversely proportion to ammonium-N recovery.

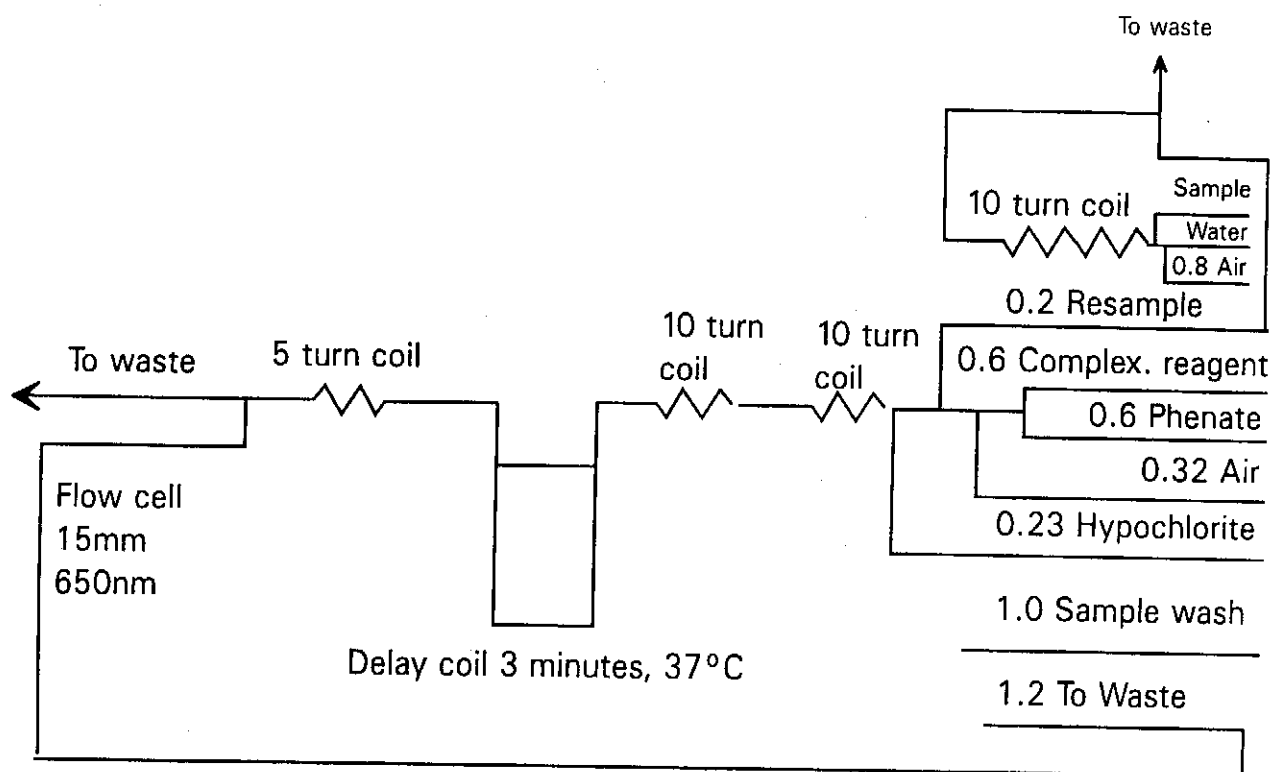


Fig. 1: AutoAnalyzer Manifold for determining $\text{NH}_4\text{-N}$

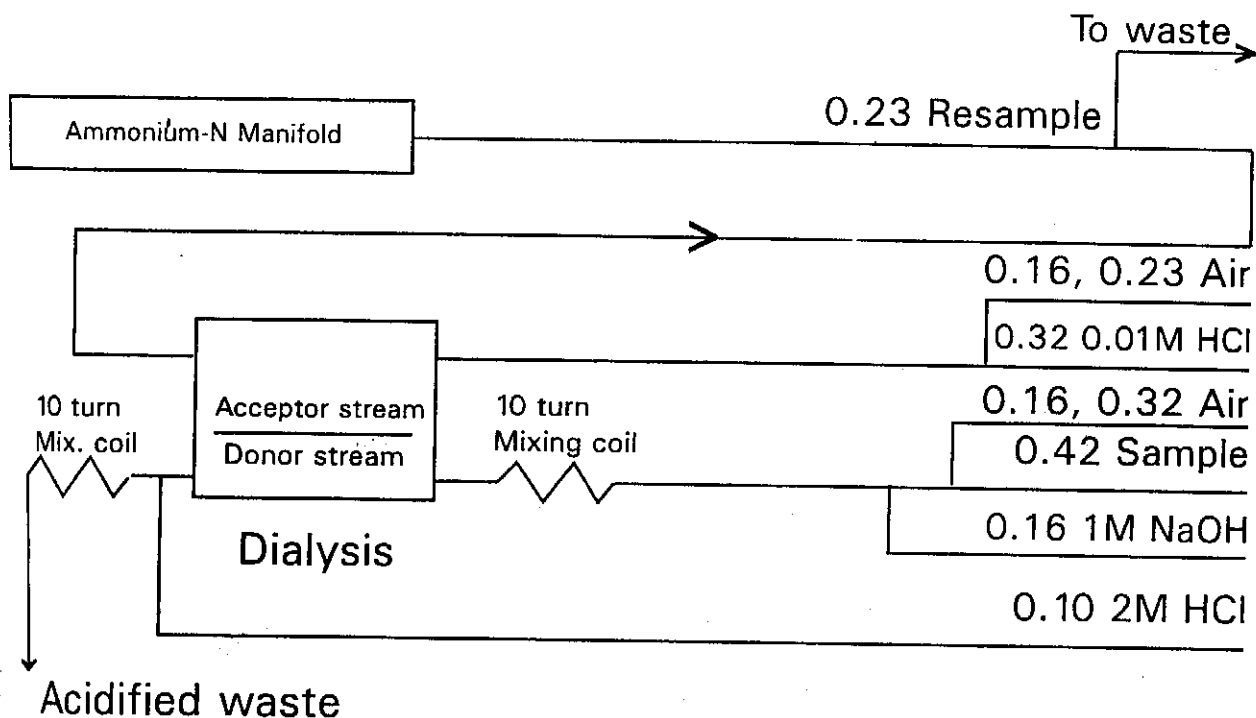


Fig. 2: Original dialysis system

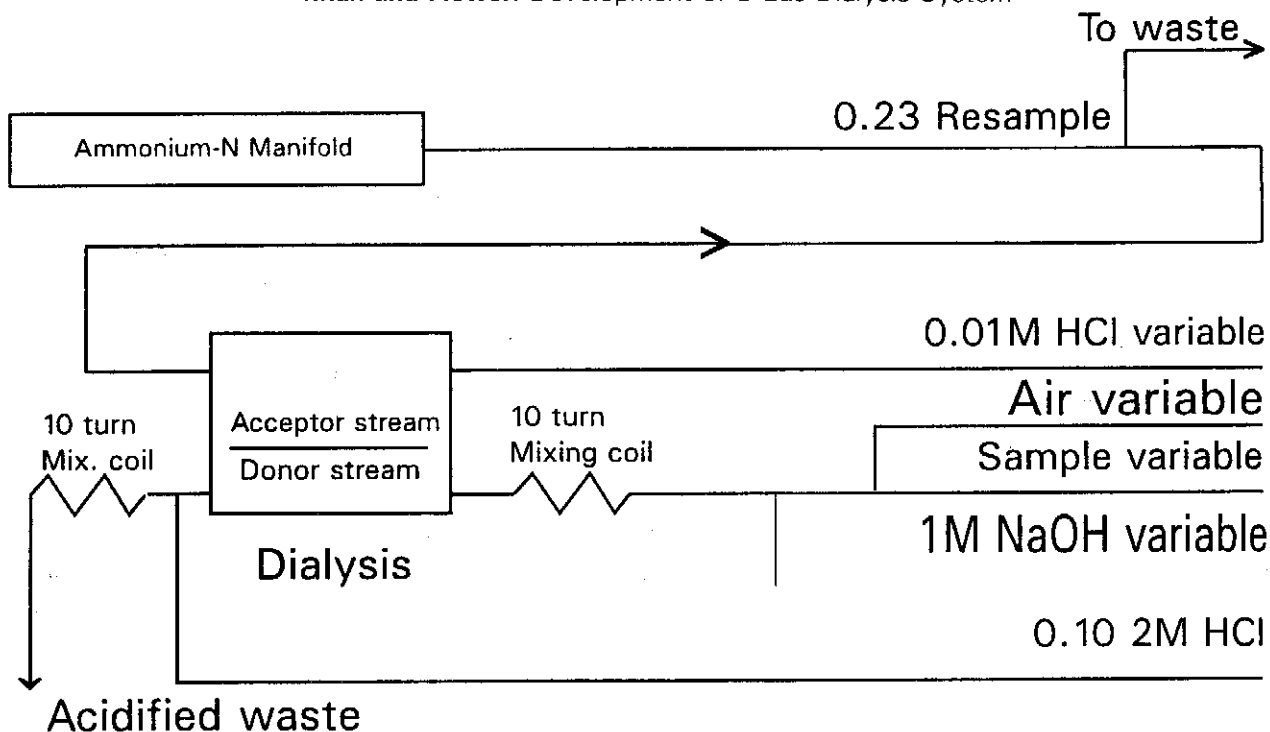


Fig. 3: Dialysis system 2

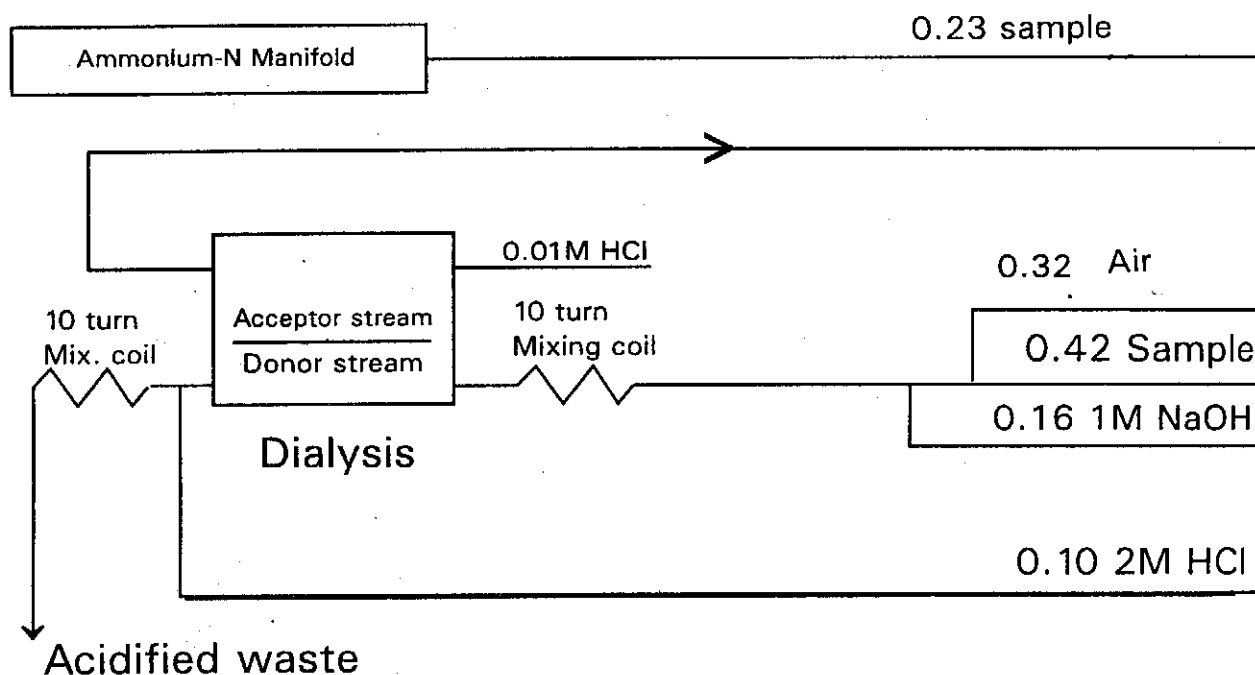


Fig. 4: Final dialysis system

Final Dialysis system: The relationship of acceptor flow rate and ammonia trapping was considered a crucial parameter for further work and the best flow rate for donor and acceptor streams was chosen to analyse the water and extracts. This led to the system shown in the Fig. 4. In this system, instead of pumping the acid acceptor stream and the resampling, the 0.23 sample line of ammonium main manifold was pulling 0.01M hydrochloric acid through acceptor side of the dialysis.

Effect of Membranes on Ammonium-N Recovery: Dialysis membranes were tested using the system shown in Fig. 4. Three and six inches dialyzers with path lengths of 15 cm and 30 cm were tested for using three dialysis membranes. These membranes were the Technicon silicon rubber gas dialysis membrane, PTFE and TFE hydrophobic membranes. The Table 4 shows the percent recovery of ammonium compared with ammonium measured by passing the dialysis step.

Table 4: Ammonium-N recovery through membranes.

Membranes	-----Dialyzers-----	
	3 inch	6 inch
	Ammonium-N recovery (%)	
Silicon	4.2	-
PTFE	59.6	86.8
TFE	53.9	81.5

Technicon silicon membrane showed very low ammonia transference. The hydrophobic membranes allowed similar amounts of ammonia to be transferred through them. Double ammonia transference was expected through 6 inch dialysis but approximately 85 percent recovery was achieved.

Effect of Samples Rate per Hour on Peak Separation: Sample rates per hour of 50, 40, 30 and 20 were tested. Analysis rate at 20 samples per hour showed improved peak separation.

Precision of the Final Dialysis System: Ammonium-N working solution (1 mg l^{-1}) was analysed using the system shown in Fig. 4 to investigate the precision of the ammonium measurement using the dialysis system with the Technicon AutoAnalyzer II method. Twelve samples of the same solution were analysed in individual sample cups. The results are shown in Table 5.

The standard deviation of the results shown in Table 5 is very low which suggests that the developed method is sufficiently precise and reliable for its use in the ammonium-N determination. Mazumder (1992) examined the ammonium-N recovery in the standard solution prepared in water (1 mg l^{-1}) in ten replicates using the Technicon AutoAnalyzer II without dialysis.

The standard deviation of the results was between 0.002 and 0.004 for a 1 mg l^{-1} $\text{NH}_4\text{-N}$ solution. Comparison of the

present results with those of Mazumder (1992) show that the present results are slightly less precise which is to be expected with the more complex system.

Table 5 $\text{NH}_4\text{-N}$ recovery of same solution

Replicate Number	$\text{NH}_4\text{-N}$ (mg l^{-1})
1	0.997
2	0.997
3	1.001
4	1.004
5	1.006
6	1.008
7	1.014
8	1.020
9	1.006
10	1.003
11	1.008
12	1.010
Mean	1.006
Standard deviation	0.0066

Linearity of the Final Dialysis System: To obtain standard calibration curves to investigate the linearity of the system, ammonium solutions (0.02 to 0.1 mg l^{-1}) and (0.2 to 1.0 mg l^{-1}) were analysed using the final dialysis system. Both calibration curves were linear ($y = 4.14 + 15.7x$, $r^2 = 0.99$ and $y = 5.11 + 42.82x$, $r^2 = 0.98$).

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