

22 Ion chromatographic determination of builders at Ecachim



The Belgian company Ecachim successfully develops recipes for different branches – day by day. Intensive research, years of experience (more than 30 years!) and a fully equipped research laboratory trusting in Metrohm instruments are the cornerstones of Ecachim's success. Thanks to Metrohm's versatile 850 Professional IC, Ecachim was able to complete their broad range of analysis techniques

Tailor-made recipes from Ecachim

Ecachim is an independent research laboratory specialized in product development and improving recipes of specialty chemicals. In their focus of interest are detergents for dishwashers, cleaners for professional kitchens or car washes, oils for the metal processing industry, additives for the construction industry, paints (e.g. for soccer field line markings), cosmetics and many more. The range of great products originating from this independent laboratory is truly amazing!

In Ecachim's field of activity, it is common knowledge that it is vital to develop new outstanding products in order to remain competitive. It is not magic that helps them in developing new recipes. Exactly the opposite is true: it is hard work to create an outstanding product. In the beginning there is always intensive research activity and the desire to understand the basics and as much of the context as possible.

Have you ever thought about how many companies, especially smaller ones, have their own fully equipped lab? In any case, Ecachim do have an efficient lab equipped with state of the art analytical instruments and capable and very knowledgeable staff to operate it. Their daily business is to conduct all necessary technical and scientific studies that serve as a basis in the development of tailor-made recipes. Although Ecachim's team is rather small, they work with great enthusiasm and are highly flexible and efficient.

Analytical techniques used at Ecachim

Over the years, Ecachim has bought a number of instruments from Metrohm; amongst them several types of pH meters and different kinds of potentiometric and Karl Fischer titrators for the determination of chlorine, acids, bases, NTA, EDTA, surfactants, etc.

A refractometer, gas chromatographs, FTIR and UV spectrophotometers, drying balances and other apparatus from different suppliers are also used during the development of tailor-made recipes. The only gap left in the analytical scheme of Ecachim was the identification and quantification of a large number of so-called «builders» contained in cleaning products. They soften the water and also help to prevent fabrics from the redeposition of dirt that has already been removed by surfactants. Of interest are not only NTA and EDTA, which both can be determined titrimetrically, or the total phosphate content, which is amenable via time-consuming



Eachim is located in Schoten (Belgium) on the river Schelde, near the industrial city of Antwerp and close to the North Sea. Antwerp is the second largest city of Belgium and hosts the country's largest port as well as the second largest chemical industrial park in the world after Houston. Crude oil, chemicals, ores, steel and cereals are the most imported commodities. The principal exported goods are petroleum products, machinery, textiles and other finished products.



Different analysis techniques are applied in the well-equipped laboratory of Eachim. Metrohm is the main supplier for instruments in ion chromatography, titration and ion measurement.

colorimetric techniques. Rather, the task consisted in determining, in one go, all the different builders, namely silicate, NTA, EDTA, citrates, phosphates, condensed phosphates (e.g. tripoly- and pyrophosphate), gluconate, sulfate, lactate, succinate, formate, phosphonates (e.g. nitrilotrimethylenetrakis phosphonic acid, NTMP, and hydroxyethylidene diphosphonic acid, HEDP).

The challenging analysis of builders

The first test using a Metrohm Compact IC for determining the builders were carried out by the team of Metrohm Belgium at the beginning of 2000. Unfortunately, Eachim's requirements could not be met as detection turned out to be difficult and separation was not satisfactory. The problem was not only the large number of compounds present in the sample but also their high concentrations ranging from 1...25% that made very high dilutions inevitable to obtain usable sample solutions. Soon it became clear that it was impossible to separate the enormous number of different compounds on a single separation column.

At the beginning of 2007, Metrohm introduced their new 850 Professional IC family of ion chromatographs. During a demonstration at the facilities of Metrohm Belgium, product manager for ion chromatography Mrs. Danny De Clerck accepted the challenge of the attending Eachim people to separate their builders once again.

Some experiments later and after giving it some thought, it was clear that the answer to the problem consisted of two separations being carried out simultaneously. The main part of the builders had to be separated on a column using high-pressure gradient elution with subsequent post column reaction (PCR) followed by UV detection.

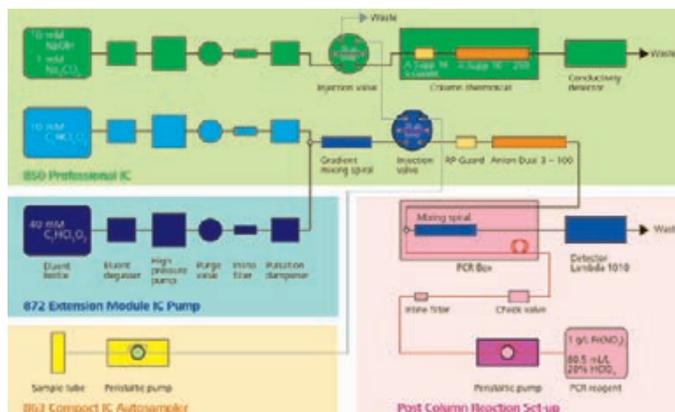


Erik Callebaut, Frank Callebaut, Danny De Clerck (Metrohm Belgium) and Anita Meynendonckx (left to right) posing in front of the Metrohm instrument for the determination of builders.

The silicates had to be separated on a second column at a moderately elevated temperature using isocratic elution and conductivity detection. Thanks to the introduction, early in 2008, of the 872 Extension Module IC Pump, which extends the ion chromatograph with an additional high-pressure pump, Metrohm Belgium was finally able to offer Eachim the analysis of builders using just one 850 Professional IC. Using the new 863 Compact IC Autosampler, this system can even be operated fully automatically.

Metrohm, a trustworthy partner

In 1978, the founder of Eachim, Erik Callebaut, started working with a very small R&D laboratory on a part-time consulting base for producers of cleaners and cosmetics. His budget was very small and therefore he was quite happy to be able to buy a used Metrohm E 415 Multi Dosimat. Although this instrument was quite old, Frank Hubrechts of Pleuger, the distributor for Metrohm in Belgium in those days, was very cooperative and still able to supply spare parts.



Schematic of the Metrohm system for the ion chromatographic determination of builders.

Ten years later, Ecachim needed a Karl Fisher titrator and still could well remember the excellent support in the past by Metrohm. Hardly surprising, they bought Metrohm's 701 KF Titrino. When Metrohm introduced its surfactant electrodes in 1998, again a couple of Metrohm instruments (mainly Titrinos and Dosimats) were purchased. For more than 30 years now, Metrohm is the main supplier for Ecachim and is held in high esteem for its reliable instruments and perfect support. Trusting in Metrohm ion chromatography to determine builders was nothing but logical.

The ion chromatographic determination of various builders in detail

This section describes in detail the method and the ion chromatographic set-up used to identify and quantify a vast number of builders in one go. The determination is performed with an 850 Professional IC specially equipped according to the requirements of the application:

- 850 Professional IC equipped for high-pressure gradients (without chemical suppression)
- 872 Extension module IC Pump
- Lambda 1010 UV/VIS Detector
- 833 IC Liquid Handling Pump Unit
- Post column reactor (6.2836.000)
- 863 Compact IC Autosampler
- 771 IC Compact Interface
- Remote Box



The 850 Professional IC is equipped with a column oven that can hold two separation columns with their guard columns. Additionally it is possible to operate a third separation column outside the oven at room temperature.

The analog measuring signal from the UV/VIS detector is converted by the 771 IC Compact Interface and then transmitted as a digital signal to the MagIC Net™ software. The Remote Box is used to control the 833 IC Liquid Handling Pump Unit that supplies the PCR reagent. The integration of an 863 Compact IC Autosampler allows the system to be operated fully automatically.

The separation of builders (except the silicates)

High-pressure gradient elution followed by post column reaction in combination with UV detection is successfully applied to separate the builders NTA, EDTA, citrate, phosphate, tripolyphosphate, pyrophosphate, gluconate, sulfate, lactate, succinate, formate and phosphonates. The silicates are not considered here but are separated according to the description below in a further separation. The following solutions and parameters have been used for the first separation:

Solutions

- Eluent A 1 mmol/L trichloroacetic acid ($C_2HCl_3O_2$)
- Eluent B 40 mmol/L trichloroacetic acid ($C_2HCl_3O_2$)
- PCR reagent 1 g/L $Fe(NO_3)_3$ in 80.5 mL/L perchloric acid ($HClO_4$)

Parameters

- Eluent flow 0.9 mL/min
- Loop size 20 μ L
- Column thermostat Not used
- Separation column Metrosep Anion Dual 3 – 100
- Guard column Metrosep RP Guard



Detailed view of the flow path with the 850 Professional IC for high-pressure gradients without chemical suppression (top) and the 872 Extension Module IC Pump (bottom).

Frank Callebaut is loading the 863 Compact IC Autosampler with new samples. Thanks to the sample changer, the system can be operated fully automatically, leading to a considerable throughput.

The separation was carried out on an Anion Dual 3 – 100 Metrosep column protected by a guard column. It is absolutely necessary to use a high-pressure gradient, here involving a solution of trichloroacetic acid at increasing concentration and therefore accelerating elution, to successfully separate such a large number of substances. Post column reaction followed by UV detection was used to exclude the interference of other anions present in the samples.

The separation of the silicates

The silicates were analyzed at the same time in the same 850 Professional IC on a separation column of the type Metrosep A Supp 16 – 250 using isocratic elution in conjunction with conductivity detection without suppression. This was achieved with the following solutions and parameters:

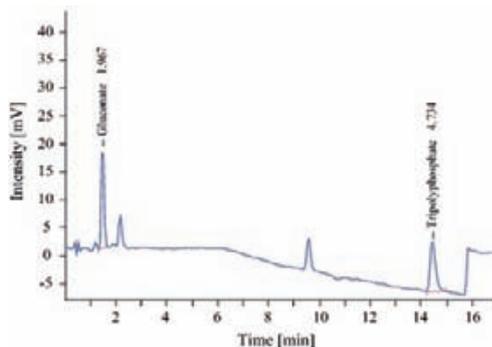
Solutions

- Eluent: 10 mmol/L NaOH, 1 mmol/L Na₂CO₃

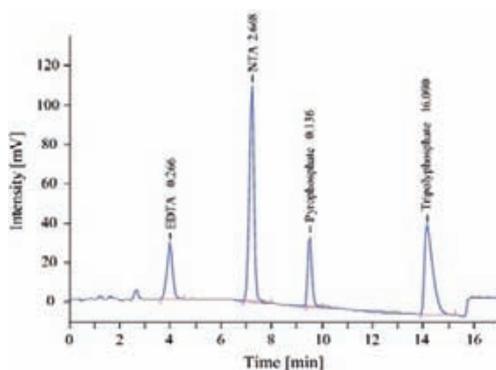
Parameters

- Eluent flow: 0.8 mL/min
- Loop size: 20 µL
- Column thermostat: set to 70 °C
- Column: Metrosep A Supp 16 – 250
- Guard column: Metrosep A Supp 16 – Guard

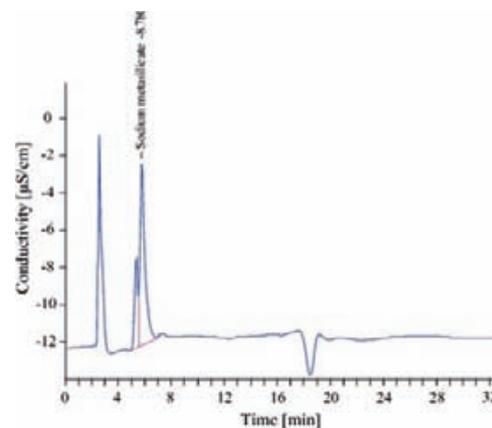
To improve the separation between the silicates and gluconate, an adapted eluent composition and a column temperature of 70 °C proved to be successful. Using the versatile 850 Professional IC from Metrohm, Ecachim is now able to fully automatically separate all their builders in one go.



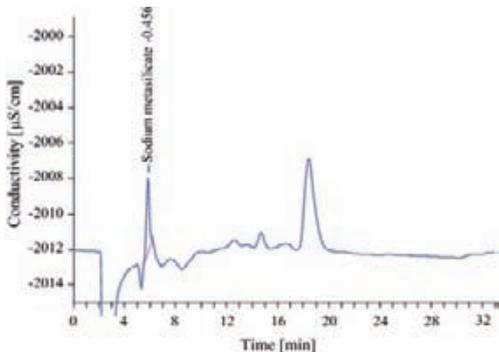
Chromatogram of sample A for the separation of gluconate and tripolyphosphate using post-column reaction and UV detection.



Chromatogram of sample B for the separation of EDTA, NTA, pyrophosphate and tripolyphosphate using post-column reaction and UV detection.



Chromatogram of sample A for the separation of the silicates and the determination of sodium metasilicate using conductivity detection without chemical suppression.



Chromatogram of sample B for the separation of the silicates and the determination of sodium metasilicate using conductivity detection without chemical suppression.