Aluminium Fractionation Techniques

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In the Manual, 'labile' aluminium is an optional parameter in soil solution, and cation exchange is recommended as the simplest and cheapest method to use. However, there are many other methods. Some are suitable for routine use, others less so.

Why aluminium fractionation?

In natural waters, aluminium occurs in many different forms, so-called species. Some, but not all, of these have a toxic effect on various organisms, including forest trees. It is thus important to know the concentrations of the toxic forms.

In general, the most toxic species are Al^{3+} and the monomeric hydroxide complexes, while fluorides, sulphates, silicates, phosphates and organic complexes are less toxic. Toxicity varies depending on organism, life stage etc.

In the case of plants, the polymer $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ is highly toxic, but it appears to be unstable under natural conditions due to interaction with humic substances, and probably does not occur very much in natural waters.

Determining the concentrations of toxic species is not easy. The different species exist in a dynamic interaction with each other that can easily be changed by adding a reagent.

Also, a reagent will react with several different species, which may or may not be toxic. Thus, what is determined during analysis is normally an operationally defined fraction (e.g. labile aluminium, quickly reacting aluminium) that must then be related to the original species. This can be done using equilibrium calculation programmes e.g. ALCHEMI.

All methods should be characterised, i.e. it is necessary to know which species are included in the measured fraction. This can be achieved by testing the method using synthetic solutions of known composition or by comparison with other, already characterised, methods (i.e. reference methods).

Characterisation has not always been done. Often assumptions (which may be wrong) are made about which species are included in the measured fraction.

Many methods can be/have been mechanised, enabling large sample throughput. These methods are suitable for routine laboratory use.

Other methods may be more suitable for research using small sample numbers.

Many analytical methods have been developed for aluminium fractionation. These can be divided up according to fractionation/determination principle as follows:

• Ion exchange (nearly always cation exchange)

• Colourimetry

• Fluorimetry

• Ion chromatography

• Electrophoresis

• Size distribution (filtration, ultrafiltration, centrifugation, dialysis, size exclusion chromatography)

• Fluoride selective electrode

• NMR

Most of these approaches have not been widely used. Some are not suitable for routine use, but have been developed for laboratory studies.

By far the most common methods in routine use involve cation exchange with either spectrophotometry or atomic spectroscopy for determination.

Ion exchange

Almost always cation exchange. Use of anion exchange is rare.

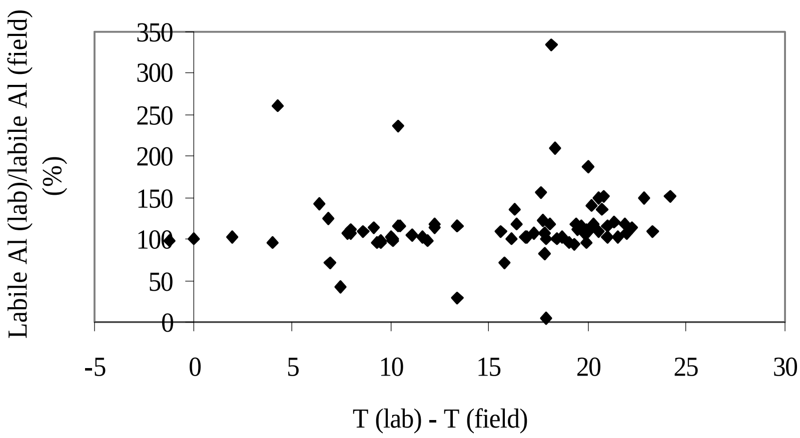
Cation exchange methods are based on the fact that the most important inorganic aluminium species are cations, while the organic species are to a large extent anionic. The most toxic aluminium species are inorganic, so these can be separated from the relatively non-toxic organic species using a cation exchange column.

The fraction that has *passed through* the cation exchange column is determined (i.e. the less toxic anionic species), and the more toxic fraction is estimated as the difference between this fraction and total aluminium.

Cation exchange has the advantage that at least two fractions are determined. One consists to a large extent of the relatively toxic inorganic species (although the less toxic fluoride complexes are also included), while the other includes the relatively non-toxic organic complexes.

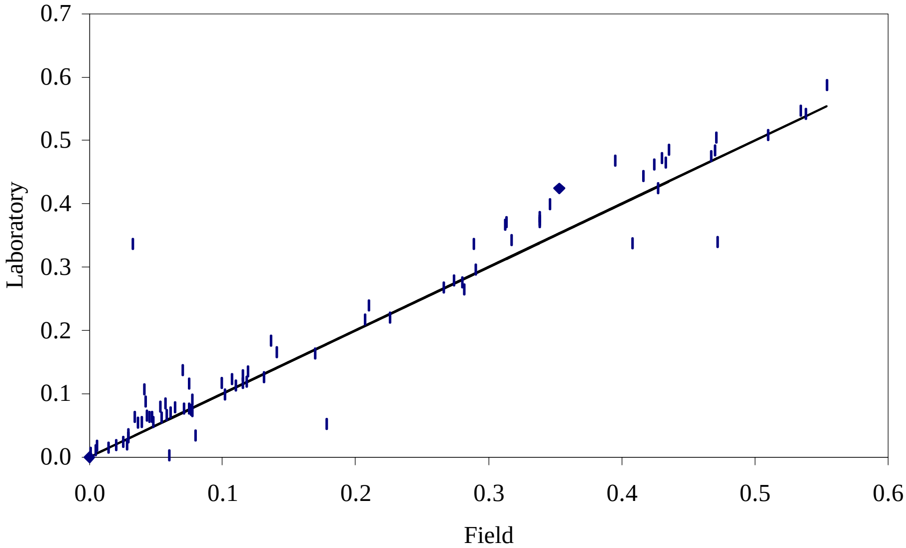
Originally labour-intensive, but mechanised versions suitable for routine analysis have been developed using flow systems.

Cation exchange methods can be easily adapted to field use. Their reaction kinetics appear to be less temperature-dependent than is the case for, for example, colourimetric methods.



Cation exchange fractionation in the field in Norway.

Comparison between labile aluminium (mg/l) determined in the field and the laboratory.



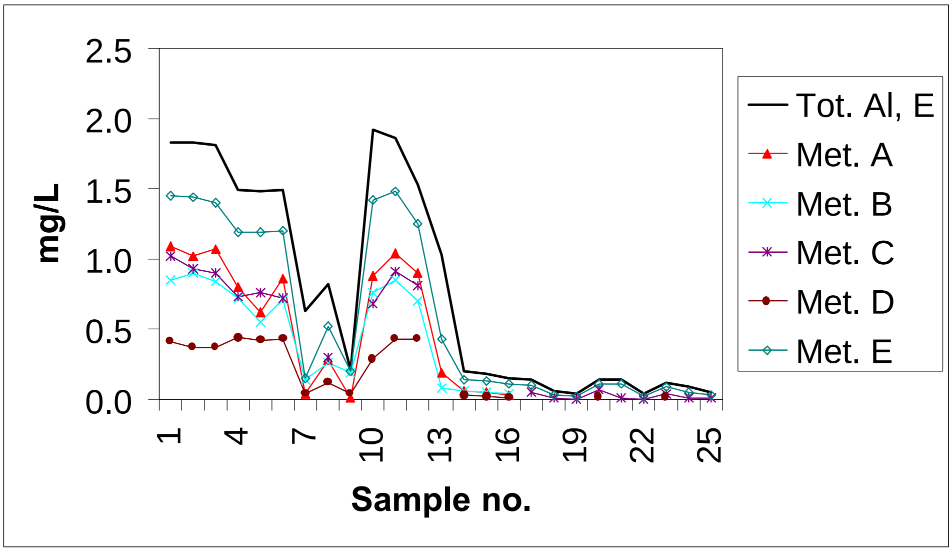
Potential problems:

• The fraction of most interest is determined as the difference between two measured fractions, increasing the error factor.

•The cation exchanger might make labile organic complexes dissociate, leading to an underestimation of the organically complexed aluminium (and an overestimation of the toxic fraction).

• Some less toxic species are cationic (e.g. AlF^{2+}).

• Different cation exchange methods do not measure the same fraction. Factors such as the type of cation exchange resin and the method of detection also influence the result.



Colourimetric methods

These methods are sometimes used together with cation exchange (as a determination step after the fractionation step), and sometimes as fractionation methods in their own right.

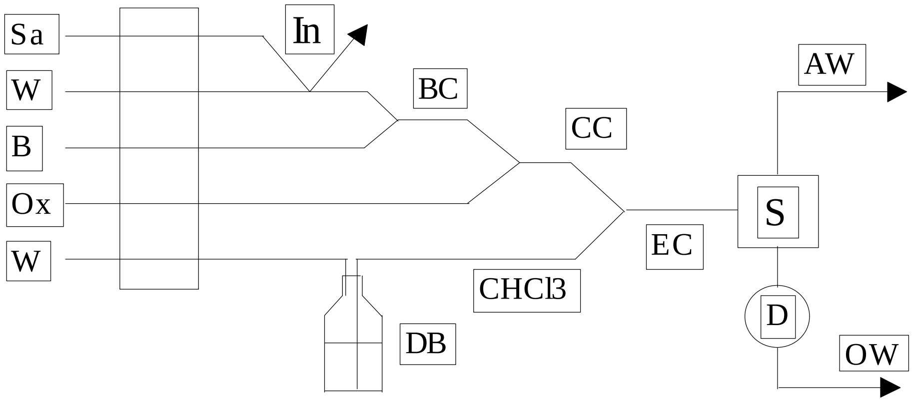
When used for fractionation, colourimetry makes use of kinetic discrimination, i.e. only the most labile or quickly reacting species will react with the reagent. Normally, simple monomeric hydroxide complexes react quickly, while large polymers and organic complexes react more slowly.

Advantage: the fraction of greatest interest (the labile, relatively toxic fraction) is determined directly, rather than as the difference between two other fractions.

Various reagents have been used:

- Pyrocatechol violet
- 8-quinolinol (8-hydroxyquinoline, oxine)
- Ferron (8-hydroxy-7-iodoquinoline-5-sulphonic acid)
- Aluminon

To be sure of what is measured, it is necessary to have good control of the reaction time, especially if this is short. This can be easily achieved using continuous flow or flow injection systems.



Sa = sample, W = water, B = pH buffer and iron masking solution, Ox = oxine solution, In = injector, BC = iron reduction and buffering coil (12 cm), CC = complexation coil (50 cm), EC = extraction coil (150 cm), S = phase separator, D = spectrophotometric detector, AW = aqueous waste, OW = organic waste, DB = displacement bottle.

Potential problems:

• Often, pH buffering is necessary as the reactions are pH-dependent. This can be a problem if pH buffering causes changes in the speciation.

• Interferences are common, especially from iron and humic substances. These problems can be dealt with using masking reagents and extraction.

• Generally unsuitable for field use as the reaction kinetics are often temperature-dependent.

• The complexing agent might desorb Al associated to particles or colloids.

Fluorimetry

A few fluorimetric methods have been developed, but these are not normally used in routine analysis.

Reagents include lumogallion, calcein blue, oxine and 8-hydroxyquinoline-5-sulphonic acid.

Problems with interferences and quenching, but these can be overcome using methods similar to those used in colourimetry.

Electrophoresis and ion chromatography

Several methods using electrophoresis or ion chromatography have been developed and used successfully to separate different aluminium species. With these methods, many different species can be detected and quantified. However, these methods are probably too time-consuming for routine analysis and there may be risks for redistribution among the species present.

Other methods

• Equilibrium dialysis is useful as a reference method (i.e. for comparison purposes), but is too time-consuming for routine use.

• Other size distribution methods have sometimes been used.

• Fluoride-selective electrodes have been used, with the assumption that all complexed fluoride is bound to Al. F-selective electrodes have been used as a reference method.

• NMR is not suitable for routine use, but has been useful for research purposes.

• Combinations of different methods have been developed to obtain a more detailed fractionation.

Which method should be chosen?

All methods have their strengths and weaknesses, and there is probably no method that is best for all purposes.

For routine laboratory use, it is best to use methods that can be mechanised, in order to give high sample throughput. Cation exchange or some colourimetric methods might be suitable.

A number of method comparisons and some reviews have been published, so it is possible to compare different methods and choose that which is most suitable.