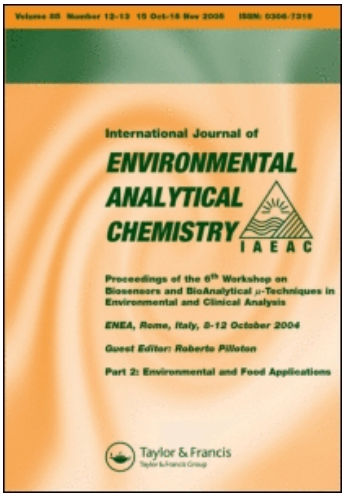

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A Novel *in situ* Cascade Ultrafiltration Unit Specifically Designed for Field Studies of Anoxic Waters

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Dedicated to Professor W. Haerdi on the occasion of his 60th birthday

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The effect of sample handling and the experimental conditions used during a filtration experiment are critical factors, which must be assessed, if truly representative size distributions of natural particulates are to be obtained. This is particularly the case when colloidal sized, reactive (coagulation, oxidation, precipitation) species such as those found in anoxic lake waters are investigated. Furthermore, such samples are generally rich in both H_2S and CO_2 and losses by volatilization may alter the pH and lead to changes in the species distribution between the dissolved, colloidal and particulate species. In this paper, we describe a submersible *in situ* cascade ultrafiltration unit which has been specifically developed to enable the study of particle size distributions *in situ*. This system has been used to investigate the particle size distributions of colloidal sized iron and manganese species in oxygen depleted and totally anoxic reduced water strata found in a well stratified hypereutrophic lake (Lake Bret, Vaud, Switzerland).

KEY WORDS: Size fractionation, *in situ* filtration, lake water, cascade ultrafiltration, particle size.

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I. INTRODUCTION

In natural aquatic media, knowledge of particle size distributions is essential if the mobility and the ultimate fate of both particulate species and adsorbed compounds is to be well understood. Size distributions are generally obtained by filtration despite a growing body of evidence that the results may be biased by operational problems.[1-6] These can become particularly acute when filtration is used to investigate particle sizes in reduced anoxic waters such as those found in eutrophic lakes. Indeed, Zumstein[7] found that when classical cascade ultrafiltration was used to fractionate an anoxic ferrous iron rich lake water sample, oxidation of Fe(II) rapidly induced filter clogging and poorly controlled conditions during the filtrations which led to non reproducible data. This was attributed to the difficulty of avoiding ingress of traces of oxygen during the sampling, sample storage and laboratory filtration sequence, despite the fact that all the steps were performed under an inert N_2 gas atmosphere.

Furthermore, even in oxic lake waters Laxen and Chandler[3] have shown that filtration based size distributions for lacustrine Fe particulates were different if the filtration was performed directly in the field or some 2–3 hours later on returning to the laboratory. Laboratory distributions were shifted to greater sizes than the corresponding distributions obtained from field data. Particle aggregation during sample storage has been proposed as being the main process explaining this shift: agitation will substantially enhance the collision rate and hence the aggregation rate. Note that, changes in the particle distribution function might not only occur during sample storage but might also occur during the sampling procedure itself—in particular when sampling anoxic waters containing reactive species—and therefore may shift field based size distributions when compared to true *in situ* distribution.

A further problem which must be envisaged when filtration is used to determine size distributions is particle interaction with the filter's surface itself and with particles trapped on the membrane. Indeed, since the life-time of colloidal particles is a function of the particle size,[8] aggregation of small colloidal sized particles onto the larger particles trapped on the filter can occur in any filtration experiment. The latter problem can however be minimized if the filtration is

performed in a cascade mode,[9] i.e., where the same water sample is successively filtered through increasingly less permeable membranes, since this progressively eliminates the larger particles. Finally, it should be noted that in order to minimize filter clogging due to polarization concentration effects[6,9] the solution should be well stirred and low flow rates should be used.

In this paper, we describe a submersible *in situ* cascade ultrafiltration unit designed to overcome or at least minimize the above-mentioned problems and enable the study of particle size distributions in totally anoxic reducing lake waters.

II. GENERAL DESCRIPTION

The *in situ* ultrafiltration unit is composed of five sub-units (see Figure 1), namely: three ultrafiltration cells, the sumbersible housing and the control box. An umbilical cord—made of 30 mm diameter reinforced PVC tubing—links the control box on the surface to the submersible unit. Through the latter cord electrical current (DC 12 V), compressed N_2 and the open-close commands to the solution and gas valves within the sumbersible housing are conveyed thus enabling the system to function *in situ*. Within the submersible housing all connections between the valves and the ultrafiltration cells were made using semi-rigid nylon tubing, with an internal diameter of 2 mm, and Swagelok fittings. Each ultrafiltration cell is held in a Plexiglass support which is attached to the housing. The nylon tubings, connecting each valve to a cell, were in each case connected to an intermediate manual tap (see Figure 1). After an *in situ* ultrafiltration and once the system had been brought to the surface, the taps were closed and connections to the housing removed. In this manner, the ultrafiltration cells containing the filtrates, now freed from the housing and isolated from oxygen contamination could be refrigerated until the necessary analyses could be performed.

II.1 Ultrafiltration cells

The three ultrafiltration cells were designed differently from classical ultrafiltration cells[10] in order to enable cascade ultrafiltration of

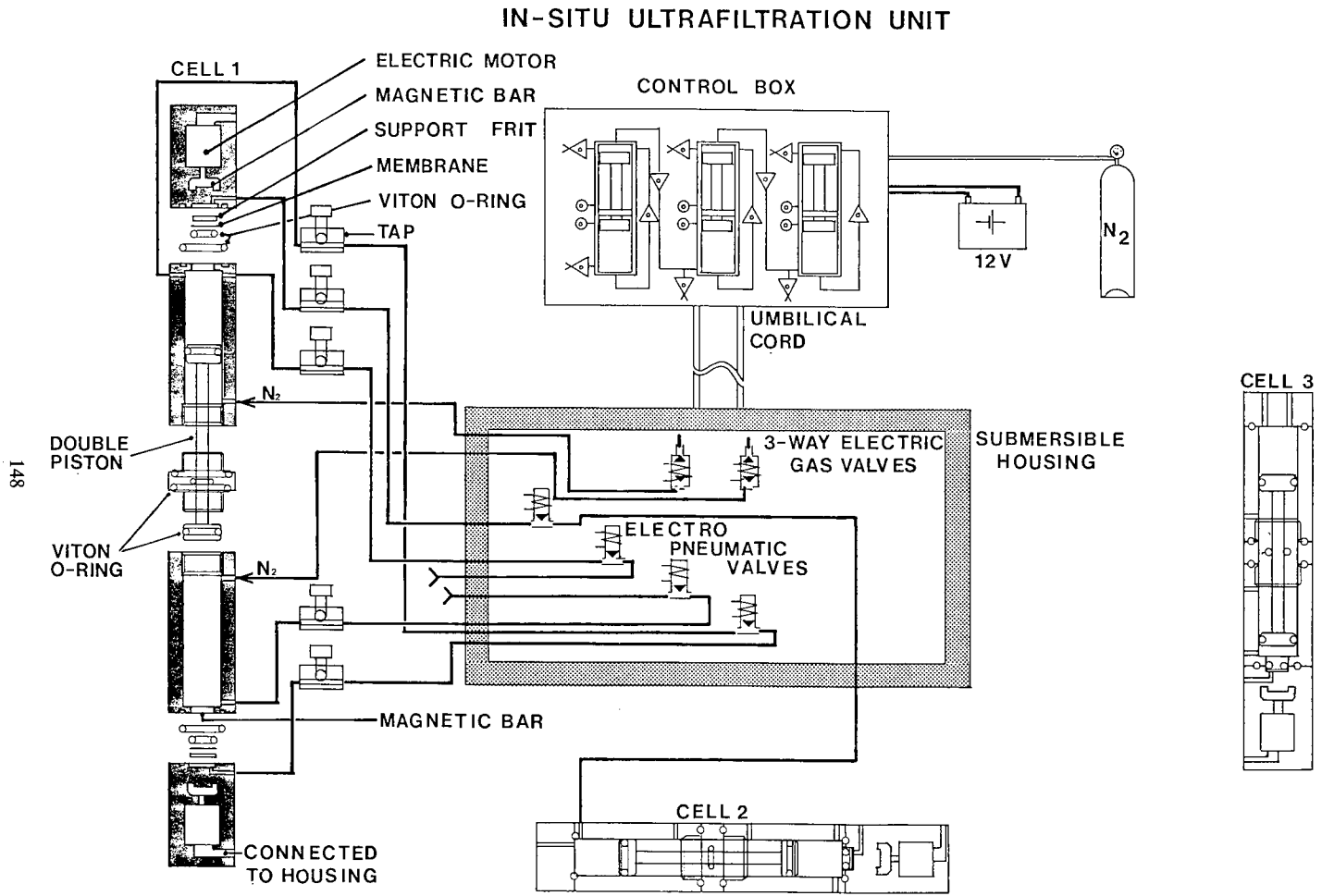

Figure 1 A schematic view of the *in situ* cascade ultrafiltration unit. On the left, an exploded view of an ultrafiltration cell.

anoxic waters which are often rich in dissolved Fe(II) and S(−II). This implied that oxygen contamination in particular had to be held to very small concentrations (less than 0.05 ppm) to avoid oxidation of Fe(II) which occurs very readily at pH 7–9. The half-life of Fe(II) has been reported to be of the order of minutes in freshwaters within the above mentioned pH range.[11] Pistons driven by N_2 pressure instead of direct N_2 pressure driven classical ultrafiltration cells have the following advantages:

a) Contact between the solution and N_2 is avoided. This is necessary since even the best commercially available N_2 (reported to be 99.999% pure) contains traces of O_2 at the ppm level.

b) *In situ* purging of the system with anoxic lake water can be readily performed, since the pistons may be used not only to push the water sample through the membrane filters but also to expel and aspirate anoxic lake water from and into each half-cell (see section III.2).

c) Sulfide losses by volatilization are less than they would have been with a classical ultrafiltration cell since there is no inert gaseous atmosphere above the solution.

Each cell is composed of two symmetrical half-cells of equal volume, through which a double headed piston can move back and forth by successively applying an N_2 gas pressure behind one or the other of the twin piston-heads. Viton O-rings were mounted on the piston-heads to ensure that no gas leaks occurred when the pistons are either at rest or in movement. At the extremities of the half-cells there is a filter assembly consisting of: a membrane filter, a support frit, and Viton O-ring. Just above the filter assembly a 28 mm magnetic bar encased in Plexiglass and held between two pins stirs the solution entrained by a primary magnetic bar and an electric motor encased at the end of the half cell. All three ultrafiltration cells were made of Plexiglass cylinders with an external and internal diameter of 60 and 35 mm respectively, they were all made to the same specifications except for two important differences, outlined below:

1) The volume of the half-cells: the filterable volume was 100 ml in cells no. 1, 80 ml in cell no. 2 and 60 ml in cell no. 3. Consequently when filtering a sample from cell no. 1 to cell no. 2, the difference in

volume i.e., 20 ml stays in the upper half-cell (labelled B in Figure 2D). This retentate hereafter referred to as fraction B can then be stored in the half-cell until analysis. Fraction C is obtained in an analogous manner. Whereas the last two fractions, D and E, are simply obtained by stopping the filtration after half of the initial volume (60 ml) has been filtered.

2) In order to be able to collect five different fractions namely A, B, C, D and E (see Figure 2D) four filtration stages are required. Two filtrations are performed in cell no. 1, and one in both cells nos. 2 and 3. Cell no. 1 is therefore equipped with a filtering system (membrane filter, O-ring, support frit and a magnetic stirrer) adapted to each of its half-cells whereas cells 2 and 3 have only one half-cell equipped.

II.2 Submersible housing

The submersible housing (see Figure 1) was also made of Plexiglass and was assembled using silicon O-rings, rubber joints, screws and Swagelok fittings and was water tight down to a depth of 20 meters. Within the housing eleven solution valves (Lucifer 131 M 74/Bachhofen 3775k) and six 3-way gas valves (Bellows Valvair G-50) are fixed on specially made Plexiglass supports. Note, that a striking feature of the electropneumatic solution valves used by us was that no direct contact between the solution and the moving parts of the valve occurs (see Figure 3). Contaminations of any sort are therefore avoided.

III. MANIPULATION

III.1 Laboratory preparation

Before using the *in situ* ultrafiltration unit in the field one should completely purge the ultrafiltration cells, the connecting tubes, valves etc., first with N_2 gas and then with degassed Milli-Q water in order to minimize subsequent contamination of the anoxic lake water sample by residual atmospheric oxygen. The complete system—the three ultrafiltration cells equipped with the appropriate membrane filters, and the submersible housing—was assembled in the laboratory and

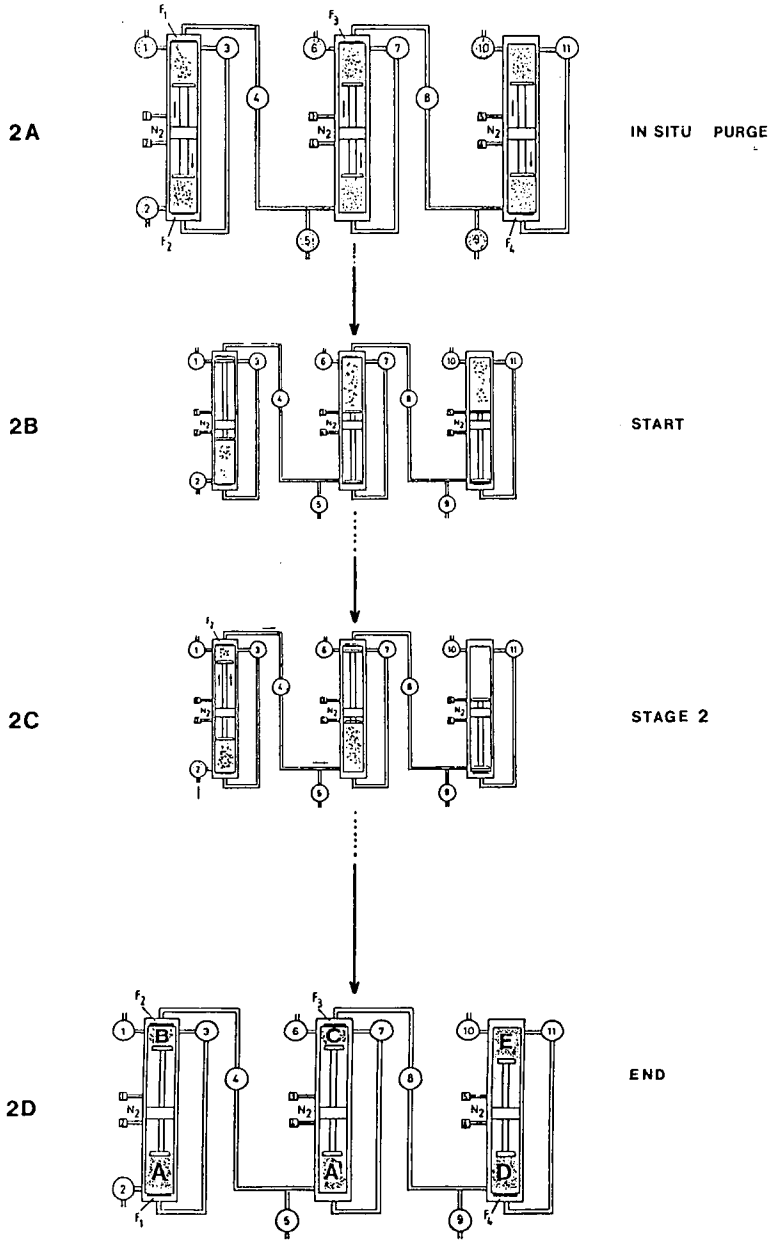

Figure 2 A pictorial representation of four of the different stage of an *in situ* cascade ultrafiltration. The position of the pistons and the fractions A, A', B, C, D and E obtained are shown in 2D.

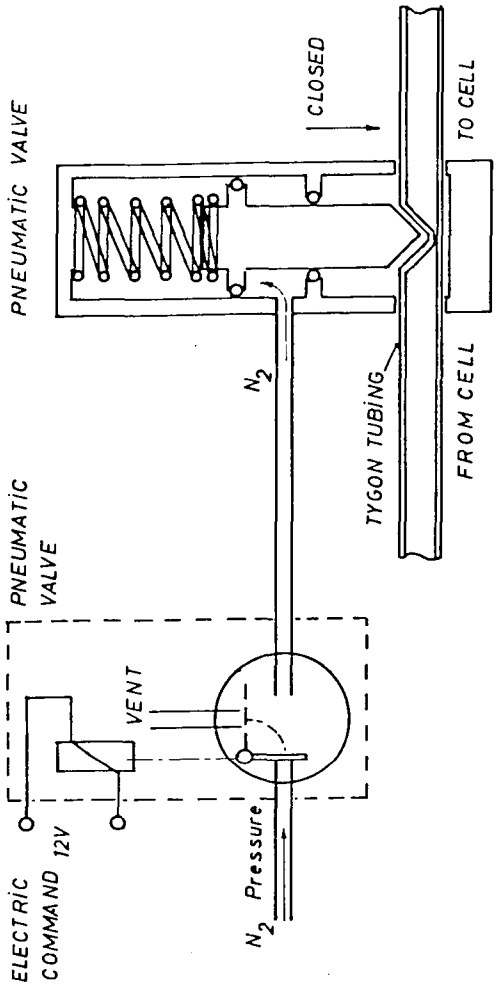

Figure 3 A schematic drawing of an electro-pneumatic solution valve, which avoids any contamination of the sample solution since no direct contact between the solution and the valve occurs.

a continuous flow of N_2 (50–200 ml/min) was flushed through the system for at least 4 hours to ensure complete deoxygenation. Degassed Milli-Q water, prepared by bubbling N_2 gas through 2 liters of water for at least 24 hours, was then slowly forced through the cell assembly using an external reservoir under N_2 pressure. At least 200 ml of Milli-Q water was passed through each filter and discarded by opening an intermediate tap, in order to eliminate possible heavy metal and organic contaminations released by the filter itself.[12] Flow rates were monitored and checked against optimal flow rates given by the manufacturers to detect any clogging or a faulty membrane. Once the system was completely filled with degassed Milli-Q water, it was disconnected from the reservoir, and all the taps were closed. The system was stored for not more than 8 hours before use in the field.

III.2 Field use

The submersible housing and its three ultrafiltration cells was lowered to a given depth in the lake, and the separation begun. The first step (see Figure 2A) is a final *in situ* purge of the system using the anoxic lake water itself to remove any residual oxygen. Each piston in each cell was successively moved backwards and forwards in order to aspirate and expel anoxic lake water into and from each half-cell. The system was then lowered to the depth at which the studied species is present, a water sample is taken into half cell A, and the filtration begun. The various filtration steps (see Table 1) carried out

Table 1 Steps performed during an *in situ* cascade ultrafiltration

Step	*Function*
In situ purge	System clean-up (elimination of O_2)
Start	Position of the pistons before the first filtration
Stage 1	Filtration through F_1
Stage 2	Filtration through F_2
Stage 2′	Solution transfer
Stage 3	Filtration through F_3
Stage 4	Filtration through F_4

in situ are schematically depicted in Figure 2 and the corresponding status of the eleven solution and the 6 gas valves in Figure 4. The position of the pistons at the end of an *in situ* cascade ultrafiltration and the fractions obtained labelled A to E are indicated in Figure 2D.

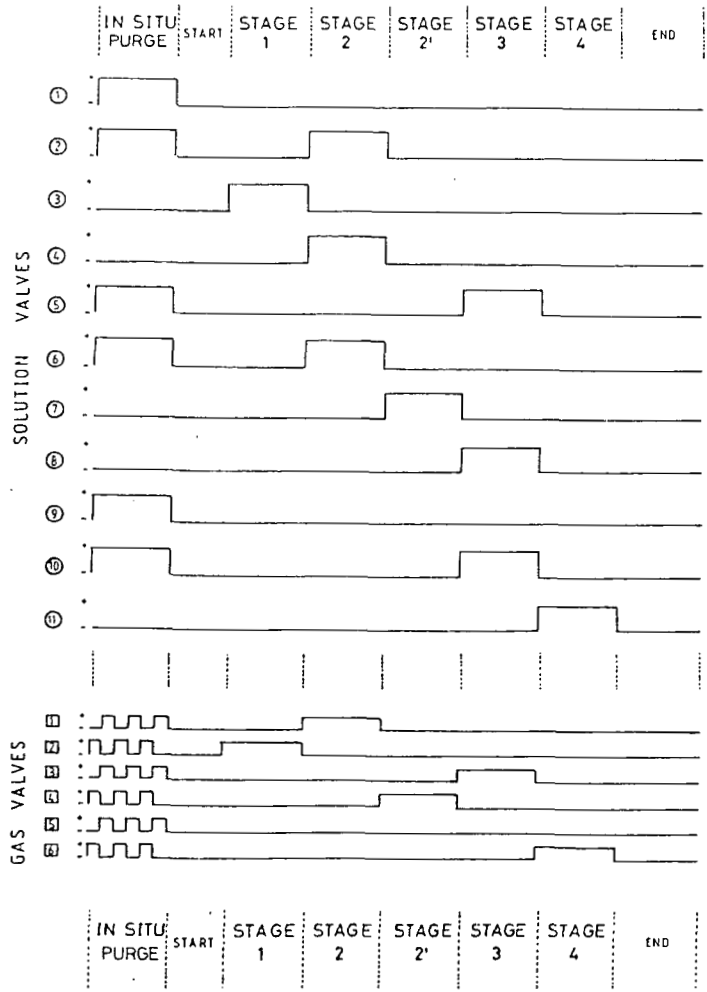

Figure 4 Status of the eleven solution valves and the six gas valves during the eight different steps performed during an ultrafiltration.

III.3 Analyses

In order to obtain a size distribution for the studied metal species, atomic absorption, colorimetric measurements and polarographic analyses were done to determine the concentrations of total Fe, Mn and Ca, total Fe(II) and electroactive Fe(II) and Mn(II), respectively. These analyses were performed on fractions A, B, C, D and E. It should be underlined that for the polarographic measurements the sample was transferred directly from the half-cell into a specially modified polarographic cell. All the sample handling and experimental procedures used are described elsewhere.[5]

III.4 Calculations

At the end of an *in situ* cascade ultrafiltration experiment and after the necessary analyses have been performed, the raw data must be converted into a size distribution. This, however, is not a straightforward calculation since a number of characteristics of the *in situ* unit must be taken into account. The overall result at the end of an experiment is schematically represented in Figure 5. Different symbols *a*, *b*, *c*, *d* and *e* have been used to distinguish different particle sizes of a given metal, *M*, whose concentrations in each of the fractions A, B, ..., E is symbolised, $|M|_{A,t}, |M|_{B,t} \ldots |M|_{E,t}$. It should be stressed that of the five fractions obtained: A is unfiltered lake water, B, C and D are fractions retained between two filters and E is the last filtrate. Fractions B, C and D however are not pure fractions as obtained using, for instance the so called washing technique,[9] but include particles smaller than the nominal pore size. Indeed, in fraction B, for instance (see Figure 5) there is no particle *a*, all particles *b* and a small amount of particles *c*, *d* and *e* which have not been removed because the volume of the cell was not entirely filtered. This of course, must be taken into account when computing the size distributions from the raw concentration data measured in the filtered samples. Equations 1–5 in Figure 5, constitute a system of five equations with five unknowns, $a, b, \ldots, e$ which can therefore be easily solved to obtain the size distribution of the investigated metal *M*. Three important remarks should however be made in this respect:

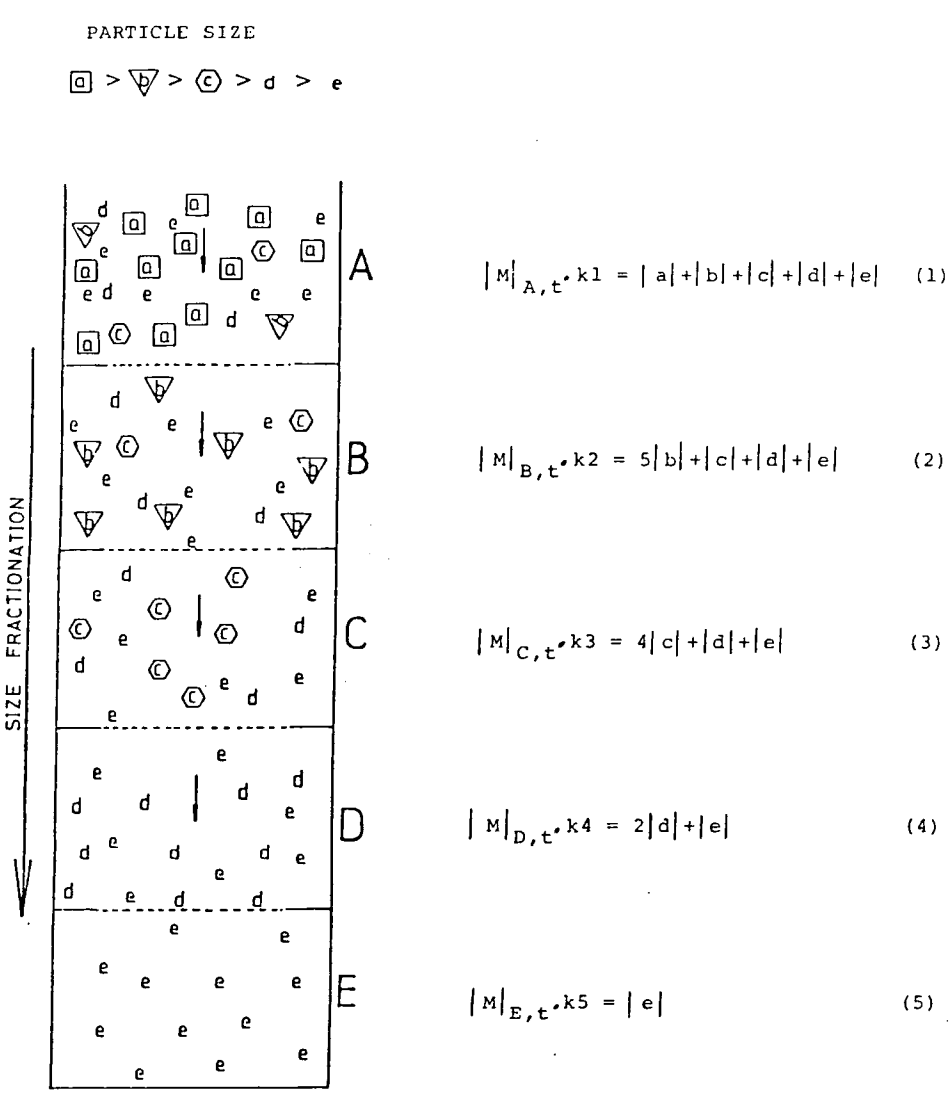

Figure 5 Schematic representation of the mode of size fractionation used to fractionate particles *in situ*. Equations 1–5 enable calculation of the concentration of particles in a given size fraction defined by the filters used.

1) In Eqs. 2, 3 and 4 the concentration terms $|b|$, $|c|$ and $|d|$ are multiplied by a constant factor of 5, 4 and 2, respectively. This may be readily understood by considering Eq. 2 for fraction B. The initial sample volume is 100 ml of which 80 ml is filtered through the membrane into cell 2. Particles *b*, which are larger than the nominal pore size of the membrane used are consequently concentrated by a factor of 5. An analogous reasoning is valid for particles *c* and *d* in fractions *C* and *D*.

2) In Eqs. 1–5, *k*1 *to k*2, are constants which correct the measured total concentrations of the metal *M* (i.e., $|M|_{B,t}$ in fraction B) to its true value by taking into account a small constant dilution which occurs during each filtration step, due to the connecting tubing, valves and dead volumes which were initially filled with degassed Milli-Q water, and which consequently progressively dilutes the lake water sample as it is ultrafiltered through the system. Values for $k1, k2, \ldots, k5$ can be computed by determining the polarographically measurable concentration of Mn^{2+} in all five samples, since Mn^{2+} must pass through all the membranes and consequently its concentration should be equal in all the fractions, if no dilution occurs. The differences observed can thus be used to compute the above mentioned dilution correction constants. Values for the latter can also be determined from the concentration of any other conservative (with regards to filtration) species, such as total calcium determined by atomic absorption.

IV. APPLICATIONS AND POTENTIAL

The *in situ* cascade ultrafiltration unit has been tested and used in the field[5] to study Fe-rich and Mn-rich particulates found in a small eutrophic lake (Lake Bret, Switzerland). The lake develops an extensive anoxic hypolimnion during the summer season and both colloidal and particulate iron and manganese species are found in the oxygen depleted waters of the metalimnion and in the anoxic waters of the hypolimnion. Some representative examples of size distributions obtained using the *in situ* unit are discussed below in order to illustrate the possible applications and potential in the *in situ* cascade ultrafiltration unit.

Two typical size distributions for a particulate Mn species found in the oxygen depleted waters (ca. 1–2 mg/l) of the metalimnion are shown in Figure 6. They were obtained by measuring the total Mn concentration and the electroactive (i.e., polarographically measurable) Mn(II) concentration in each of the ultrafiltration fractions A–E. Simultaneous use of two analytical techniques, namely atomic absorption and differential pulse polarography (DPP) enables one to make a distinction between electroactive and non electroactive Mn within the size distribution (see Figure 6). Note, that electroactivity is also related to size since it may be shown that the size of an electroactive species has to be necessarily smaller than ca. 50 nm.[13] It is important to include the above-mentioned distinction since many authors have in the past considered that total Mn concentrations determined in a 0.45 μm filtrate could be safely assumed to be aquated Mn^{2+}. In Lake Bret, this is clearly not the case, since approximately 35% of the non electroactive Mn is found within the 0.015–0.1 μm size range (Figure 6).

The *in situ* cascade ultrafiltration unit has also been used in a study of the particle size distribution of iron rich particles found in the metalimnion of Lake Bret. Two different filtration modes were used: *in situ* cascade filtration and direct field filtration. In the latter case, polypropylene syringes equipped with Swin-lok 25 mm filter holders were used. These filtrations were performed directly in the field, on sampling, and in each case a new lake water sample was directly filtered through the appropriate filter. Iron was determined by atomic absorption in the filtrates and a size distribution computed. The two modes of filtration are compared in Figure 7, where a shift towards larger sizes is apparent in the field syringe based distribution compared to the *in situ* cascade size distribution. This shift may be due either to aggregation effects during the sampling procedure or during the filtration itself and/or due to polarisation concentration[9] leading to gel formation. This latter effect might be very important with syringe filtrations which are performed at large flow rates and without stirring. It may be shown that these factors are critical if representative reproducible results are to be obtained.[6] The size and chemical composition of these Fe species has also been investigated using Transmission Electron Microscopy and Energy Dispersive Spectroscopy.[14] Direct measurement of the least diameters of the Fe rich particles on the electron

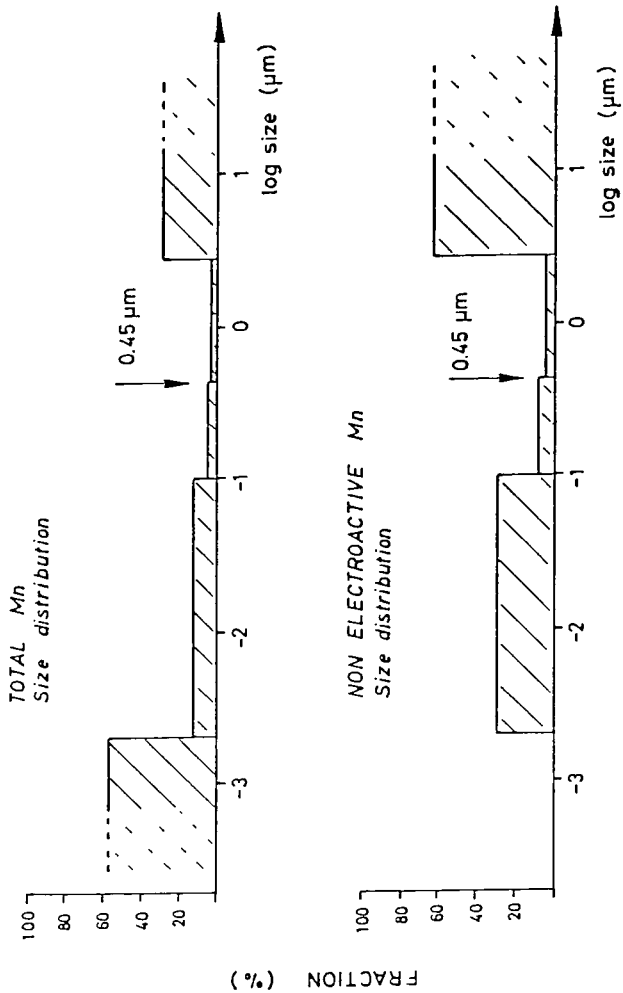

Figure 6 Mn size distributions, for both total Mn and non electroactive Mn obtained using the *in situ* cascade ultrafiltration unit. Lake Bret, 13.5 meters depth, 22 May 1985.

micrographs showed that the size of more than 90% of the particles is in the range 40 to 300 nm, i.e., a range which fits much better with the *in situ* cascade filtration results than with those obtained by syringe filtration (see Figure 7).

A third and final example of the usefulness of the *in situ* cascade ultrafiltration unit is the size fractionation of a particulate Fe(II) species found in the deeper waters of the hypolimnion of Lake Bret which are rich in both aquated Fe^{2+} and dissolved sulfide. In this case, three filtration steps were used and each ultrafiltration fraction A, B, C and D was analysed for iron using three different analytical methods: atomic absorption for total Fe, a colorimetric technique for total Fe(II) and DPP for electroactive Fe(II). As it can be seen in Figure 8A the combined analytical data obtained in each fraction shows that:

a) In all the fractions the total Fe concentration is equal to the total Fe(II) concentration, indicating that no Fe(III) is formed during the filtration due to oxygen contamination.

b) The concentration of electroactive Fe(II), after correction for dilution is identical in all fractions, confirming that no contamination by O_2 occurred and more inportantly, that the *in situ* filtration unit enables one to work with anoxic very reduced lake water samples.

Size distributions relative to total Fe and total non electroactive Fe based on this data are given in Figures 8B and 8C, respectively. As for Mn the simultaneous use AAS and DPP enables one to distinguish between the latter two forms and to consequently obtain more precise data as shown in Figure 8C.

In conclusion, we wish to underline the necessity of taking into account the operational nature of most filtration based size distributions unless the separation is performed *in situ* using a cascade mode of filtration such as the one we have developed. This is particularly so when reactive chemical systems such as those found in anoxic natural waters are studied. Such systems are best described as steady state, non equilibrium, kinetically controlled chemical and biological systems, which may consequently be expected to change during any sampling and sample storage procedure, leading to artefacts in the size distributions. In the future, a more reliable

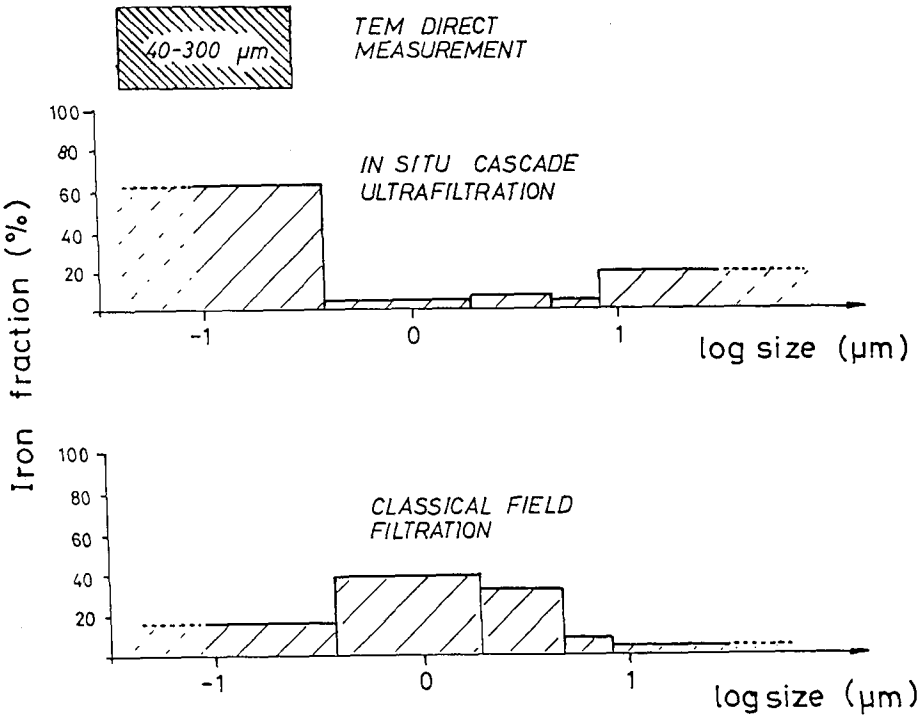

Figure 7 Comparative Fe size distributions, obtained by Transmission Electron Microscopy (TEM), *in situ* cascade ultrafiltration and classical field filtration using syringes equipped with filter holders. Nuclepore filters with nominal pore sizes of 8, 5, 3 and 0.4 μm were used. Lake Bret, 14 metres depth, 2 July 1985.

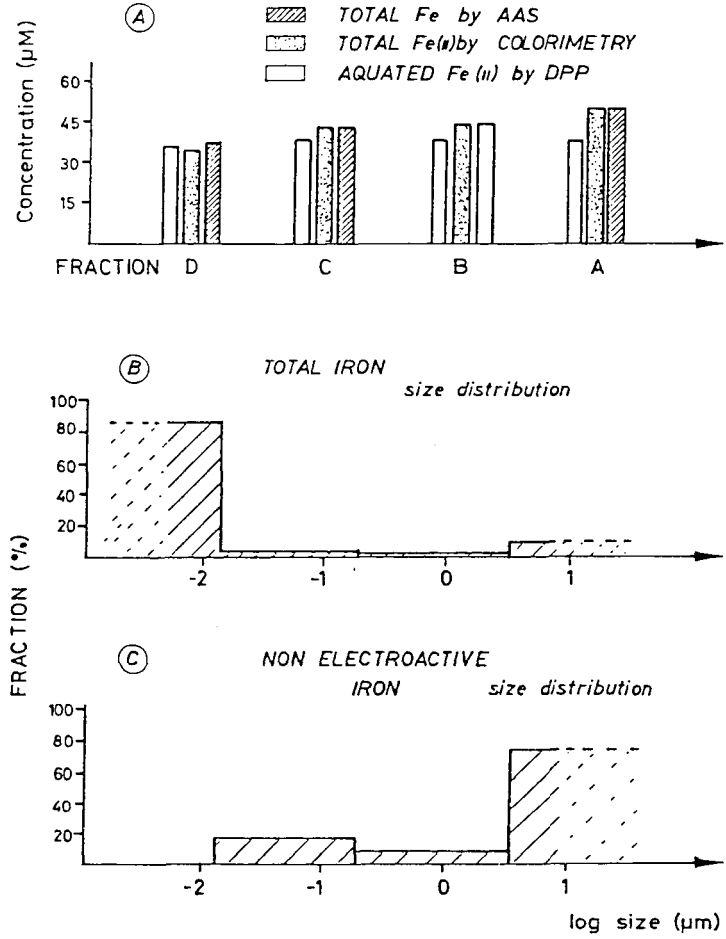

Figure 8 (A) Analytical data obtained from an *in situ* ultrafiltration within the hypolimnion of Lake Bret at 13.5 meters depth on the 2nd of October 1985. Nuclepore filters with a nominal pore size of 3 and 0.2 µm and an Amicon XM 300 with a molecular cut-off of 300,000 were used in this experiment. (B) and (C) size distributions for total and non electroactive iron, respectively computed from this data.

knowledge of the size distribution of Fe and Mn particulates in anoxic waters and consequently their fate, can in our opinion only be obtained if *in situ* techniques similar to the one described here are developed and if the filtration is performed using well controlled conditions.

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