Supplementary material

On-line separation and determination of trivalent and hexavalent chromium with a new liquid membrane annular contactor coupled to inductively coupled plasma optical emission spectrometry

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S1. Hollow fiber membrane contactor

One of the most important problems in designing and implementing hollow fibre contactors [1] is fixing the fibres to the modules.

In our contactor at the end of the large fibers, Tefzel ferrules (ETFE, Upchurch Scientific Oak Harbor, WA, USA) were used to give them the appropriate conic shape. The seal was obtained by means of Viton O-rings (external diameter = 1/4 in; internal diameter = 1/8 in) (Fig. S1) by applying pressure with a polytetrafluoroethylene (PTFE) disc suitably perforated to allow the flow of the membrane solution and the passage of small fibres.

The small fibres were anchored to two 6-mm-thick poly-isobutylene disks, which also function as a separator of the waterproofing chamber of the feed and membrane solutions. To obtain the necessary seal on the disks, the fibre ends were strengthened by introducing a thin steel needle of approx. 1 cm. The correct placement of the fibres in the septum was achieved by syringe needles for veterinary use with a suitable diameter, because when inserted into the septum, they can receive the fibres inside them and once withdrawn, can release them in the right position.

This fixing system allows the length of the fibres to be easily controlled so that the coaxial configuration was respected. The PTFE supports, which allow the fixing of the fibres and the introduction of solutions into the contactor, assure chemical inertia, easy assembly and perfect sealing, obtained with Viton O-rings (external diameter = 1 in; internal diameter = 3/4 in).

The external periscopic part of the glass was realized to reactivate a good alignment of the fibres, which tend to swell in contact with organic membrane solvents, after loading the solutions.

The supply of solutions inside the contactor was obtained by connecting the tubes of the peristaltic pumps to the connection tubing made of stainless steel, which was screwed into various PTFE parts, suitably perforated. To improve sealing, the interstices in the steel/PTFE interface were filled with a suitable filler (Frenafiletti Forte 327, Saratoga, Milan, Italy).

S2. Optimization of the ICP-OES parameters

In the on-line mode, the influence of the replicate read time was evaluated to obtain the most repeatable signal. This has been changed from 5 to 20 s, observing an improvement in repeatability of the measurement for a time of 20 s (Fig. S6). Longer acquisition times were not taken into account because they were not considered compatible with the practical application of the system.

It should be noted that passing from the reading of the input solution to the reading of the output solution is necessary to exclude at least four measurements, corresponding to the rinse time needed for the transfer line of the sample to the torch.

Based on these graphics, the elaboration of the signal for the analytical determination of Cr(III) and Cr(VI) was established. Since the points before the step, concerning the measurement of the input solution of the contactor, correspond to the Cr_{TOT} and the points after the step, relative to the output solution of the contactor, correspond to Cr(III), the step height corresponds only to the Cr(VI). Then, the variation of the ratio between the intensity of the Cr signal and the intensity of the signal of the internal standard corresponding to the step was chosen as the instrument signal.

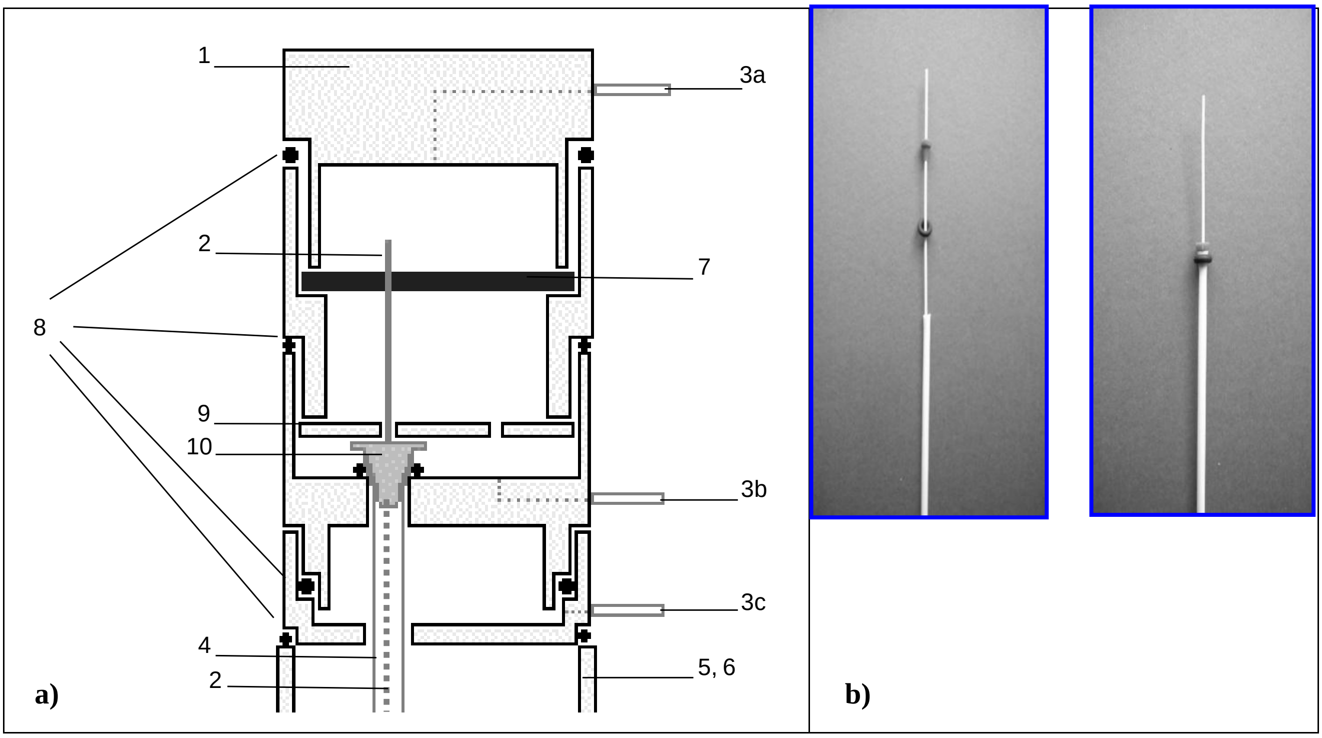

Figure S1. a) Scheme of the upper end of the annular contactor. 1, 1') stopper (in polytetrafluoroethylene, PTFE); 2) first hollow fiber with a smaller diameter; 3a,b,c, 3'a,b,c) threaded spouts (in steel) for the feeding (inlet/outlet) of the feed, receiving and membrane solutions; 4) second hollow fiber with a larger diameter; 5, 6) cylinder (glass) with a smaller or larger diameter; 7) perforated disc (in polyisobutylene) for the separation between the receiving solution and the membrane solution when the receiving solution flows inside the first fibers with a smaller diameter vice versa for the separation between the membrane solution and the source solution when the solution source flows within the first fibers with a smaller diameter; 8) o-ring (in Viton); 9) perforated disc (in PTFE) to support the first fiber with a smaller diameter; 10) ferrule with o-ring (in Viton). b) Detail of the fibre fixing system.

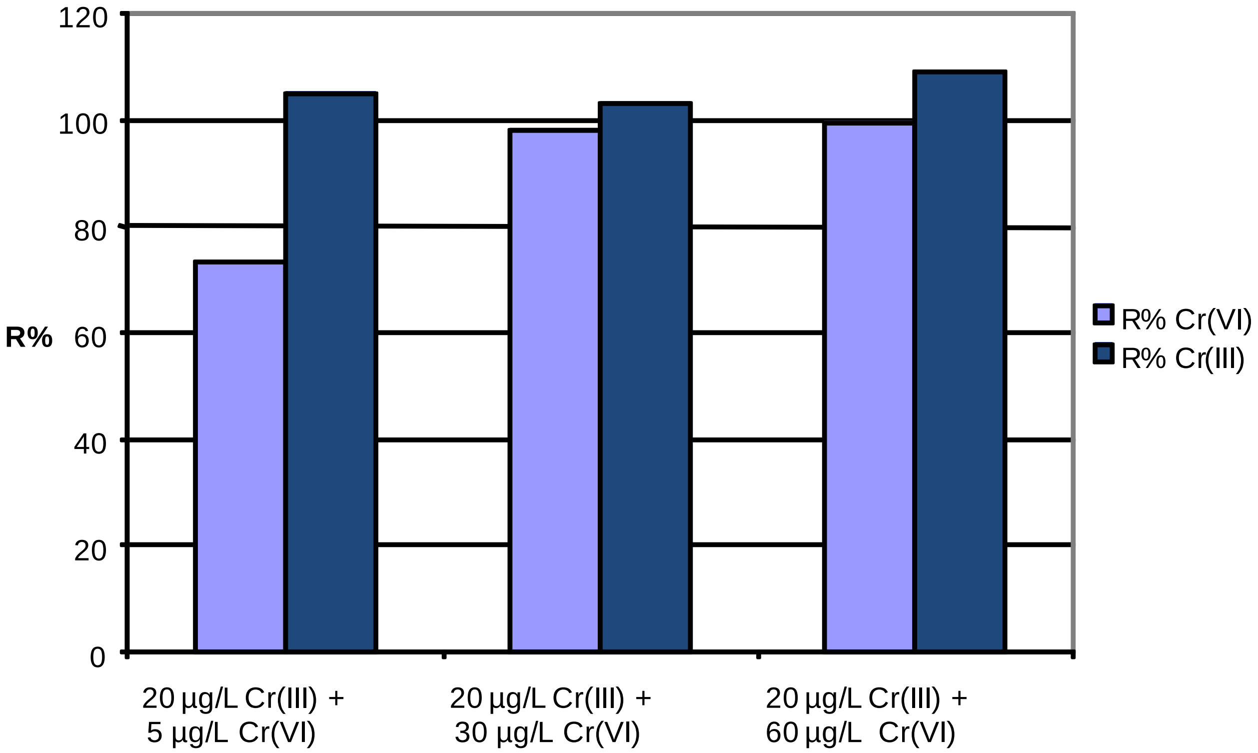

Figure S2. Percentage recoveries (R%) using standard solutions.

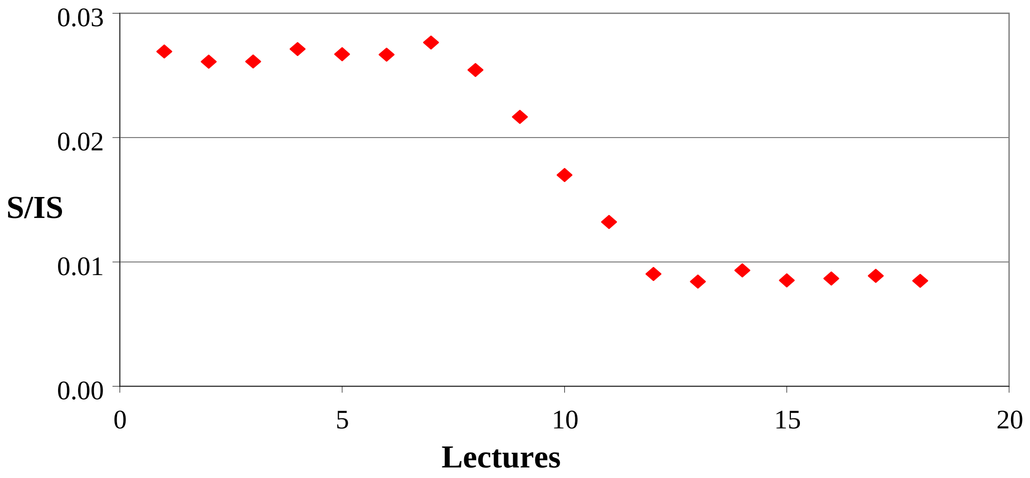

Figure S3. Signal of the analyte (S) relative to the internal standard signal (IS) according to the number of readings with replicate read time of 20 s; [Cr(VI)]initial = 60 μg/L, [Cr(III)]initial = 30 μg/L.

Reference

1. A. Gabelman, S.-T. Hwang, Hollow fiber membrane contactors, J. Membrane Sci. 159 (1999) 61–106.