Flow Injection-Flame Atomic Absorption Spectrometric Determination of Trace Levels of Cadmium with on-line Preconcentration by Means of Coprecipitation

by Rong Wei Min* and Elo H. Hansen**

Chemistry Department A, Technical University of Denmark, Building 207, DK-2800 Lyngby, Denmark

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Flow injection systems for determination of trace metal ions are described, which comprize on-line preconcentration by coprecipitation with ensuing dissolution and detection by flame atomic absorption spectrometry. Exemplified for the assay of cadmium, which is coprecipitated with iron(II) by means of hexamethylene ammonium hexamethylene dithiocarbamate in an incorporated knotted reactor and subsequently eluted by an organic solvent of methyl isobutyl ketone, two optional FI-approaches for accomplishing this feat are compared and discussed in respect to performance. While one, which is based on a previously published procedure, employs continuous pumping of the eluting agent, the approach suggested herein relies on dissolution of the collected precipitate within a small, discrete organic zone. Because the concentration of analyte thus is increased in the eluent, this concept allows an increased sensitivity, a lower limit of detection (0.074 µg l⁻¹; 3σ), and an extended dynamic measuring range (0.5-20 µg l⁻¹), albeit implying an increased sample consumption per assay and hence a decreased sampling frequency.

Opisano uklady do wstrzykowej analizy przeplywowej (FIA) do oznaczania sladowych ilosci metali, wykorzystujace zatezanie on-line przez wspolstracanie, rozpuszczanie i detekcje za pomocą pomocy płomieniowej atomowej spektrometrii absorpcyjnej. Jako przykład przedstawiono oznaczanie kadmu poprzez współstracanie z żelazem(II) za pomocą heksametylenoditiokarbaminianu heksametylenoamoniowego w węczelkowym reak-
In many environmental or biological matrices the concentration levels of several transition metals are so low that these samples, after having been brought into solution following appropriate acid digestion, are below the detection limits of conventional flame atomic absorption spectrometry (FAAS). Therefore these determinations either require the use of graphite furnace atomic absorption spectrometry, or that the samples are preconcentrated prior to analysis [1,2]. A few years ago Fang et al. [3] described a flow injection (FI) approach comprizing an ingenious preconcentration procedure by means of which trace amounts of lead ions could be determined by FAAS via on-line precipitation with hexamethylene ammonium hexamethylene dithiocarbamate (HMA-HMDTC) as facilitated by coprecipitation with a surplus of iron(II) ions. Based on a batch procedure originally outlined by Eidecker and Jackwerth [4,5], Fang et al. [3] in their on-line modification of the process collected the precipitate at the inner wall of knotted reactor made of microline tubing without using a filter, and subsequently dissolved the precipitate in a stream of methyl isobutyl ketone (MIBK) which was directly introduced into the burner of the FAAS-instrument. Under optimized conditions, coprecipitation of lead and collection of the precipitate in the knotted reactor was found to be quantitative. In a subsequent and very detailed investigation, Welz et al. [6] extended this approach to assay of cadmium, cobalt and nickel in biological samples, exploiting that HMA-HMDTC forms compounds of low solubility with numerous transition metals. Therefore, if the main component [here iron(II)] in a mixture of transition metals forms the compound of highest solubility, and the other elements are present only at trace levels, it is sufficient to add a small amount of complexing agent in order to get partial precipitation of the main component. This precipitate then acts as a collector which coprecipitates all the less soluble trace elements.

For their system Welz et al. [6] used a manifold as that depicted in Fig. 1. As is seen (Fig. 1a), sample solution [to which is added iron(III) at a fixed concentration level of 200 mg l⁻¹] is first mixed with ascorbic acid in order to reduce the iron quantitatively to iron(II), and subsequently merged with the HMA-HMDTC solution, giving rise to the generation of precipitation in the knotted reactor (KR). During this sequence MIBK, as delivered via the displacement bottle (B), is constantly fed to the nebulizer of the FAAS instrument. In the dissolution stage (Fig. 1b), pump P1 is stopped, and the position of the directional valve (V) is shifted to guide the MIBK-solution through the knotted reactor. The precipitate is hence dissolved and fed to the FAAS instrument.
Figure 1. FI manifold for on-line coprecipitation/dissolution as used by Welz et al. [6]. V – injector valve; P1 and P2 – peristaltic pumps; B – displacement bottle (the black area at the top represents the screw-on cap); C – reduction coil; KR – knotted reactor (collector); W – waste; FAAS – flame atomic absorption spectrometer; (a) precipitation stage and (b) dissolution stage (redrawn from ref. 6)

This approach yielded impressive result — thus for the assay of cadmium it was possible, at a sample consumption of 2.7 ml as delivered by time aspiration, to obtain an enrichment factor of 24 and an enhancement factor of 52, a detection limit (3σ) of 0.15 μg l⁻¹ and a relative standard deviation of 1.5% for a level of 10 μg l⁻¹, although the dynamic measuring range was rather limited (2–10 μg l⁻¹ for cadmium) [6]. The constant propulsion of MIBK during the dissolution stage implies, however, that the eluted precipitate during its travel through the manifold to the detector is prone to dispersion which in turn resulted in the formation of rather low peak signal responses, the heights of which also were low compared with their widths. Besides, the shifting of the valve from the precipitation-stage (Fig. 1a) to the dissolution-stage (Fig. 1b) necessarily implied that a residual aqueous phase (from the KR collector) became sandwiched between the pure MIBK solution and the eluting stream of this solvent. Being the principal cause of the rather unstable base prior to the emergence of the recorded signal, this aqueous phase also manifested itself in a significant background signal due to the reagents used for coprecipitation [6].
It was therefore decided to attempt to examine this approach more closely, partly in order to investigate the effectiveness of the organic eluent with the aim of trying to limit the volume required to dissolve the precipitate and hence to limit the dispersion of the sample within the FI-conduits, which in turn should lead to improved peak signal outputs; and partly in order to find out if alternative designs of the FI-manifold would be beneficial in terms of extending the detection limit and the dynamic measuring range, and possibly provide a more versatile system. From an operational point of view it would also be preferable if the consumption of the MIBK eluent, due to its toxic effects, could be minimized, although one can take advantage of the fact that the FI-system is a closed one.

This required a redesign of the system suggested by Fang et al. (Fig. 1), that is, with one comprising a second directional valve and an auxiliary pump as depicted in Fig. 2 (cf. Procedure). This communication discusses the results obtained and the performance achieved by the alternatively designed system, and whether the added complications, as compared with the previously suggested system, might justify its practical applicability.

EXPERIMENTAL

Instrument

A Perkin-Elmer model 2100 atomic absorption spectrometer equipped with a deuterium lamp background corrector was used without an impact system (flow spoiler or impact bead) in the spray chamber. The HCl-lamp for cadmium was operated at 8 mA. The wavelength was set to 228.8 nm. The lowest possible acetylene flow rate for a stable burning flame of 1.8 l min$^{-1}$ was used with an air flow rate of 10 l min$^{-1}$. The nebulizer uptake rate was adjusted to give optimum response for conventional sample introduction resulting in an uptake flow rate of 6 ml min$^{-1}$.

A Perkin-Elmer Model FIA-200 flow injection system was connected to the flame atomic absorption spectrometer with 70 cm of 0.5 mm i.d. PTFE tubing (b, Fig. 2). The optional fiveport rotary valve (similar to the one depicted in Fig. 1) was used to control the flow direction during the precipitation and dissolution stages. The actuation times of the injector valve (V1) and of the two incorporated peristaltic pumps (P1 and P2), and the flow rates delivered by the pumps as determined by their rotational speed (rpm), were programmed on the attached computer of the instrument. The third pump (P3), which was operated continuously, was a peristaltic pump (Mini-S-840, Ismatec, Switzerland). The auxiliary valve (V2) was a 6-port rotary valve furnished with an external sample loop [7]. The time resolved absorbance signals recorded were displayed on the monitor screen, and were printed out together with the absorbance values on an FX-80 printer. A time-constant of 0.5 s was used for all peak evaluations. All pump tubes were of Tygon. A displacement bottle (Tecator AB, Sweden [8]) was used to deliver the MIBK as this solvent is incompatible to Tygon. Water was pumped through the inlet tube which extended to the bottom of the displacement bottle, and the organic solvent was displaced from the top layer through the outlet tube at a nominally identical flow rate.

The small premixing coil (C) was made of 0.7 mm i.d. PTFE tubing, while the knotted reactor/precipitate collector (L1), the external sample loop (L2) and all connecting tubes consisted of PTFE tubing of 0.5 mm i.d. and 1.8 mm o.d. The knotted reactor was made by tying interlaced knots with the smallest possible diameter loops (about 5 mm). For comparison, also a knotted reactor consisting of PTFE tubing of 0.5 mm i.d. and 1.0 mm o.d was tested.
Reagents and standard solutions

All reagents were of analytical reagent grade quality, and distilled water was used throughout. Hexamethylene ammonium hexamethylene dithiocarbamate (HMA-HMDTC) solution, 0.2%, was prepared fresh each day by dissolving 200 mg of the reagent in 100 ml of water containing 0.5 ml of 5% (m/v) of lithium hydroxide.

Ascorbic acid, 2%, was made fresh each day by dissolving 2 g of ascorbic acid in 100 ml of 0.2 mol l\(^{-1}\) aqueous potassium chloride solution containing 7.5 ml of 0.2 mol l\(^{-1}\) hydrochloric acid. Iron(III) solution, 10.0 g l\(^{-1}\) Fe, was prepared by dissolving 48.406 g of iron(III) chloride hexahydrate in water and diluting to 1 l.

Standard solutions of cadmium were made by appropriate dilutions of a 1000 mg l\(^{-1}\) stock solution with 0.1 mol l\(^{-1}\) nitric acid as the diluent. All standards were made to contain 200 mg l\(^{-1}\) iron(III) by adding the appropriate amount of the 10.0 g l\(^{-1}\) iron(III) stock solution.
Procedure

The FI-manifold for the on-line coprecipitation and dissolution is shown in Figs. 2a and 2b, respectively. It consists of three pumps (P1–P3), one of which (P3) continuously feeds nitric acid (0.1 mol l\(^{-1}\)) to the nebulizer of the FAAS-instrument thereby ensuring a constant and stable baseline signal, while the other two pumps and the two injection/directional valves (V1 and V2) are operated sequentially according to the scheme depicted in Fig. 3. With valve 1 in the inject-position and valve 2 in the fill-position, pump 1 is initially activated for 20 s, which primarily serves to fill the sample line with fresh sample in order to ensure that the previous sample solution is completely replaced so that any possible carry-over between samples is eliminated. During this sequence, the flow from pump 1 is via valve 1 propelled directly to waste. After these 20 s, pump 1 is stopped and pump 2 is activated, and, with the valves remaining in the same positions, water is, at a pumping rate of 2.0 ml min\(^{-1}\), directed to the displacement bottle B for 10 s resulting in a flow of MIBK through the sample loop L1 of valve V1 and via line b led to the waste outlet of valve 2. This is equally well a cleansing procedure to ensure rejuvenation of the system prior to the actual loading. Pump 2 is then stopped, valve V1 is turned into the fill-position and pump 1 is restarted, which initiates the actual sampling cycle (Fig. 2a). Sample solution [with Fe(III) added] is premixed with ascorbic acid in coil C (30 cm), in which iron(III) is reduced to iron(II), and via valve V1 directed into sample loop L1, which consists of a tightly knotted PTFE reactor (300 cm). Immediately following the valve, the sample stream is confluenced with HMA-HMDTC solution, the combined stream subsequently being guided through the length of sample loop L1, where precipitation of iron and coprecipitation of cadmium take place. The depleted sample/re-

![Figure 3. Time sequencing of the three peristaltic pumps (P1–P3) and the two injection/directional valves (V1, V2). For the pumps the bold lines denote operation, while the thin lines refer to stop periods. The numbers are times in seconds. For the valves the bold lines signify that the valve is in the fill-position, while thin lines refer to inject-position. Vertical thin lines designate valve switches.](image)

![Figure 4. Zone sequencing during the dissolution stage. The preprecipitated sample material in the collector tube (L1) is dissolved in the small (40 µl) organic zone (MIBK sample diss.) sandwiched between two aqueous zones, that is, the large depleted sample solution and an injected small slug (20 µl) of sample solution (Aq. sol.). The sample containing organic zone is subsequently entrapped in loop L2 of valve 2 and injected into the FAAS instrument.](image)
agent solution is led to the waste outlet of valve 1. After 140 s (corresponding to a nominally introduced sample volume of ca. 7.0 ml), pump 1 is deactivated. During the last 12 s of this time frame pump 2 is simultaneously operated at a nominal flow rate of 3 ml min⁻¹. This step, where MIBK is directed through the bypass of valve V1 and via line b led to the waste outlet of valve 2, is mainly to ensure that the flow-rate delivered from the displacement bottle is absolutely constant. After this time period, valve 1 is turned into the inject-position, thus providing access of MIBK to sample loop L1 (Fig. 2b). Pump 2 is kept operating for an additional 6 s (again at a nominal flow rate of 3 ml min⁻¹). However, due to the precipitate formed in the reactor the back-pressure in this conduit becomes increased, and therefore the actual flow rate through L1 is considerably less than the nominal flow rate. In fact, the volume of MIBK solution introduced during these 6 s is only ca. 40 μl [yet reproducibly metered from cycle to cycle, because the precipitate formed predominantly is due to the presence of iron(II), the level of which is identical in all samples]. When pump 2 is stopped, valve 1 is shifted into the fill-position and pump 1 is restarted for a short period of 2 s (at half the nominal pumping rates of before – cf. Fig. 2a), whereby a small slug of aqueous sample/reagent solution (ca. 20 μl) is positioned behind the MIBK zone. After this operation, the valve is returned to the inject-position, and while pump 1 is stopped pump 2 is restarted and let to run for an additional 30 s at a reduced speed of 1.0 ml min⁻¹ in order to ensure that dissolution of any remaining precipitate in loop L1 is effected. As a result of these manipulations, the zone sequencing entering line b (70 cm), and subsequently reaching valve 2, will be that shown in Fig. 4, that is, in front will be pure MIBK followed by a large zone of depleted sample/reagent solution, the small 40 μl slug of MIBK which during its path through loop L1 has dissolved the precipitate, a small aqueous sample/reagent zone (ca. 20 μl, as a result of the 2 s valve switching) and finally pure MIBK. By the action of pump 2, this train of zones is guided towards and through the external loop L2 of valve 2, which loop has a volume of 40 μl. At the very time that this loop is filled with the MIBK-sample zone (easily identified by the adjacent aqueous solutions), valve 2 is switched to the inject-position (insert in Fig. 2b) and the sample is carried to the nebulizer by the nitric acid solution. After the loop has been emptied, the valve is turned back to the fill-position, whereby the ensuing flow of pure MIBK can cleanse the conduits in preparation for the next measuring cycle.

RESULTS AND DISCUSSION

As pointed out by Fang et al. [3], the knotted reactor (L1) has two important functions in the on-line coprecipitation system. Firstly, it promotes radial mixing of sample and reagent, providing reproducible conditions for the precipitation, and secondly, it acts as a collector of the precipitate. In this context, the material of the collector tube (knotted reactor) plays a significant role for obtaining quantitative or near quantitative retainment of the precipitated material. Fang et al. found that the best results were obtained with Microline tubing of 0.5 mm i.d. Since the precipitate is formed on the walls of the collector tube, the length of the reactor expectedly had a much more pronounced effect on precipitate collection than on precipitate formation as the latter is extremely fast. In fact, a linear relationship between peak response and reactor length was observed when the length of tubing was less than 100 cm, while for longer lengths the ensuing recorded absorbance signal gradually approached a constant value, implying completeness of precipitation and precipitate collection. For that reason, the authors settled for a tube length of 150 cm, which length proved to yield more than 95% collection efficiency. Fang et al. also pointed out that PTFE tubing of similar dimensions (length and internal diameter) caused the peak absorbance to decrease to about half of that obtained with Microline tubing.
However, when selecting tube material for the knotted reactor in the system presented herein, it is important to bear in mind that this system differs from that presented by Fang et al. in one important aspect. Thus while these authors use a long organic segment, as obtained by pumping this solvent for an extended period of time, in order to dissolve the precipitate formed, the present system employs a small, discrete zone of MIBK of merely 40 µl to accomplish the very same feat (cf. Fig. 4). Therefore, it is vital that this small zone, in which the precipitate is dissolved, remains absolutely intact throughout its travel in the entire system. For this reason Microline tubing, although superb for precipitation, proved to be an unfortunate choice as collector tubing, because the hydrophilicity of this material invariably caused small droplets of organic solvent to be separated from the bulk of the zone during its movement. The same phenomenon was also observed for tube materials such as polypropylene. However, PTFE tubing turned in this instance out to be absolutely ideal due to its hydrophobicity. Experimentally it was found that the absorbance signal increased with increasing length of the collector tube (L1), and leveled off around 300 cm, which was therefore selected as the ultimate choice. It is noteworthy that this figure is in very good agreement with the results of Fang et al. [3] who, for collector tube dimensions of 150 cm (0.5 mm i.d.), found that PTFE tubing gave ca. half the absorbance signal of that of Microline tubing. In this context it should be mentioned that it has been asserted that a significant parameter for collection efficiency is the diameter of the interlaced knots of the reactor [9]. Thus, smaller knots should yield better efficiency. This was, in fact, confirmed in this investigation where PTFE reactors of similar length (150 cm), identical inner diameter (0.5 mm), but different outer diameter (1.8 and 1.0 mm) were compared. Thus a reactor made from an 1.0 mm o.d. tubing, which inherently allowed the reactor to be interlaced in smaller knots (of ca. 3 mm diameter) yielded approximately 30% better efficiency than an 1.8 mm o.d. tubing (knot diameter ca. 5 mm). However, the PTFE tubing of thicker wall thickness is from a practical view point preferable because it is virtually impossible to create any constrictions in this conduit, which might be the case when using PTFE tubing of thinner wall thickness. Therefore it was decided to opt for the 1.8 mm o.d. tubing in this study and to compensate for the collection efficiency by prolonging the length of the reactor.

In order to illustrate the operational differences between the two different tube materials, Fig. 5 show the results of two experiments, performed with the system of Fig. 2 where the collector tube consisted of 300 cm (0.5 mm i.d.) of Microline and PTFE, respectively, and the volume of the loop of valve 2 was 40 µl (cf. below). However, in addition to only injecting in each experiment the 40 µl discrete MIBK-sample zone, the ensuing MIBK-wash solution (cf. Fig. 4) was divided into 40 µl aliquots which were also injected. Thus the first peak in each series corresponds to the “real” 40 µl sample zone, while the others peaks represent sample material contained in the wash solution. Obviously, the organic sample zone of the PTFE tube results in a much higher peak response than the Microline collector, actually ca. 70% higher. While any remaining precipitate not dissolved by the sample zone subsequently is collected by the first 40 µl aliquot of wash solution in case of the PTFE reactor, as represented by the ensuing single peak, this is not the case for the Microline
reactor. In fact, it gives rise to a series of gradually decreasing peaks indicating that the dissolved precipitate is distributed along the organic segments. The reason for this is to a large extent due to the fact that while the small organic elution zone when using the PTFE tubing remains an entity throughout the system and exactly matches that volume subsequently entrapped in and injected by valve 2, this does not hold true for the Microline tubing. Despite the relatively low pumping rate during the elution stage (1 ml min⁻¹) the discrete organic phase tends to be partially broken up during its path through the Microline reactor owing to the hydrophilicity of this material. Therefore, the (first) 40 µl volume segment subsequently entrapped by valve 2 will in this instance consist of the main bulk of the organic zone plus droplets of aqueous phase. These aqueous droplets are also present in the following organic segments which account for the apparently, comparatively slower wash of the system.

![Graph](image.png)

**Figure 5.** Readouts for a 20 µg l⁻¹ Cd sample as obtained with the FI system in Fig. 2 where the collector tube (knotted reactor) consisted of (a) 300 cm of 0.5 mm i.d. Microline tubing and (b) 300 cm of 0.5 mm i.d. PTFE tubing. The first peak in each experiment corresponds to the dissolved sample material contained within the discrete 40 µl MIBK sample zone, while subsequent peaks represent additionally dissolved sample material collected by ensuing 40 µl MIBK-aliquots

Having settled for a length of loop L1 of 300 cm (corresponding to ca. 600 µl), the volume of the small slug of organic solvent, and hence the dimensions of the external loop (L2) of valve 2, were established. This volume was selected as a compromise between on one hand keeping it as small as possible, yet at the same time ensuring that it had sufficient capacity to dissolve as much of the precipitate as possible, and on the other hand allowing that this volume repeatedly and exactly could be metered by the system despite the backpressure created in L1 during the precipitation stage. The optimum volume was experimentally selected to be 40 µl, which with due reference to the internal volumes of the conduits of valve 2 (totally ca. 5 µl) prompted loop L2 to be 18 cm of 0.5 mm i.d. PTFE tubing.
When Welz et al. [6] designed their system they made a very thorough investigation of the experimental operational conditions, that is, reagent compositions and pumping rates. With initial considerations given to these parameters, the composition of the reagents and the pumping rates used in the present system were established by means of a combination of a modified simplex procedure and univariate optimizations. As to reagent concentrations these investigations resulted in the following conditions (the figures in parentheses are those recorded by Welz et al.): HMA-HMDTC: 0.2% (0.25%); ascorbic acid: 2% (1%); iron(III) added to each sample solution: 200 mg l⁻¹ (200 mg l⁻¹); and nitric acid: 0.1 mol l⁻¹ (not used by Welz et al. in their system). The flow rates used in the two systems are apparent by comparing Figs. 1 and 2.

A significant difference between the two systems—besides the fact that the system presented herein employs a small organic sample slug in which the precipitate is dissolved—lies in the precipitation time. While Welz et al. found it sufficient to use a loading time of 40 s at a sample flow rate of 4 ml min⁻¹ (corresponding to nominally 2.7 ml sample solution), the present system requires 140 s sample loading at 3 ml min⁻¹ (i.e., nominally ca. 7 ml). This is not surprising keeping in mind that PTFE has an approximately 50% lower “retaining capacity” than Microline tubing [3]. However, it also implies that because the entire sample cycle is ca. 3 times longer for the present system, its sample throughput is also 3 times lower than that described by Welz et al. On the other hand, it also entails some advantages. Thus, a calibration run of samples in the concentration range 0.5–20 µg l⁻¹ yielded a straight line relationship with a regression equation of \( A = 0.0401 + 0.0201C \), where \( A \) is the recorded signal in absorbance units and \( C \) is the concentration in µg l⁻¹. The regression coefficient was 0.996, and the detection limit (3σ) was 0.074 µg l⁻¹. The precision of the method, as estimated by measuring a 10 and a 20 µg l⁻¹ standard 10 times, was found to be 9.90±0.18 and 19.99±0.35 µg l⁻¹, respectively, corresponding to relative standard deviations of 1.81% and 1.75%, respectively. As compared with the results of Welz et al., who found a linear relationship in the concentration range 2–10 µg l⁻¹ with a regression equation of \( A = -0.001 + 0.011C \) \( (r=0.999) \), a detection limit (3σ) of 0.15 µg l⁻¹ and a RSD of 1.5% at a level of 10 µg l⁻¹, it is seen that the dynamic measuring range is extended, the sensitivity is increased, the detection limit is improved, and the RSD is approximately of the same order. However, the blank value for the suggested system is higher. Whether this is due to baseline off-set caused by changing the flame conditions during the introduction of the organic solvent into the nitric acid carrier, or it is due to trace impurities of cadmium in the coprecipitating agent [iron(III)], is difficult to ascertain, but the former reason does very likely play a distinctive role.

When comparing the dissolution efficiency, the present system proved to dissolve ca. 81% in the small organic zone. This can be evaluated from Fig. 5b, where it is seen that practically all sample material is contained in the first two peaks. Assuming this holds true, their areas can be calculated to constitute 81% and 19%, respectively. This compares to an overall efficiency of 95% reported for the system described by Welz et al. which utilizes the continuous pumping of MIBK, that is, a much longer organic dissolution segment. Both systems thus entail individual advantages. At first
glance the proposed system appears to be more complicated to manipulate – which however is not a problem with modern computer-operated systems. Besides, the manual switching of valve 2 (which approach to a large extent possibly accounts for the somewhat higher RSD value as compared with that obtained by Welz et al.) might readily be automated. For instance, by adopting the approach outlined by Lindgren and Dasgupta [10], who employed an injection valve fitted with a pair of conductivity sensors at the fill and drain parts of the valve, which sensors directly could ascertain when an organic zone (as sandwich between two aqueous zones) were positioned in the the sample loop of an injection valve. Such an approach would very likely also entail an enhanced precision as compared with the manual operation of valve 2. An added advantage is also the reduced consumption of MIBK, which in the originally proposed system is pumped continuously, but the ultimate choice of system approach is more to be dictated by individual requirements. It remains therefore to be seen whether the alternative suggested herein will merit further applications.

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