(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 May 2004 (13.05.2004)

PCT

(10) International Publication Number
WO 2004/040292 A1

(51) International Patent Classification[7]: G01N 27/416, 27/49

(21) International Application Number: PCT/CZ2003/000063

(22) International Filing Date: 30 October 2003 (30.10.2003)

(25) Filing Language: Czech

(26) Publication Language: English

(30) Priority Data:
PV 2002-3611 1 November 2002 (01.11.2002) CZ

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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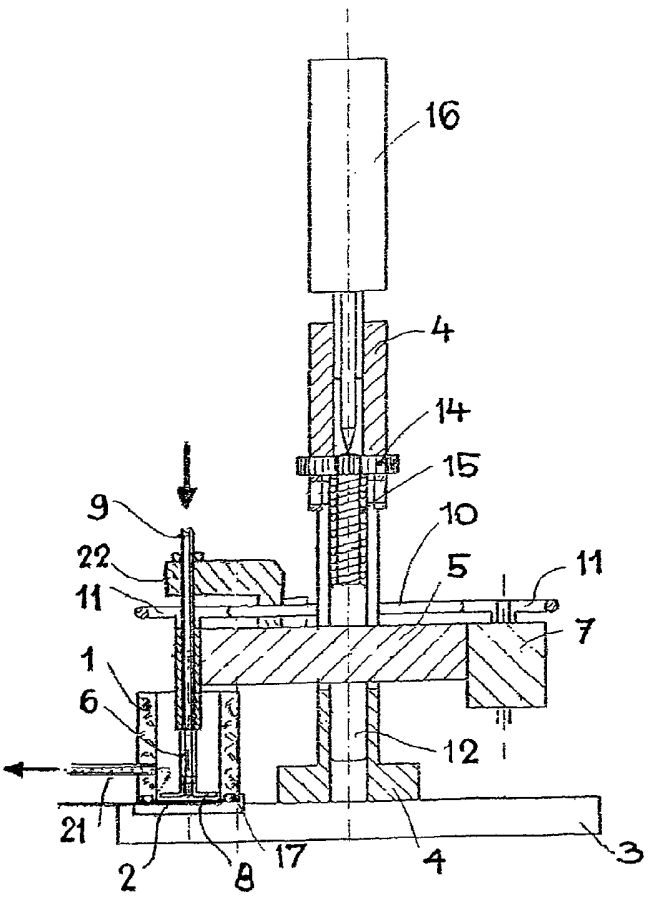
(54) Title: EQUIPMENT FOR CHEMICAL ANALYSIS



(57) Abstract: For chemical analysis of water solution of samples there is designed an equipment comprising an electro-chemical planar sensor (2) which is an integral part of at least a bottom and/or cover (22) of the measuring cell and comprise means for adjustment of conditions of hydrodynamics within the measuring system having a distribution body (8) which is rotateably seated and engages with means for its rotation.

WO 2004/040292 A1

Published:

— *with international search report*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

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EQUIPMENT FOR CHEMICAL ANALYSIS

Technical Field

The invention relates to equipment for chemical analysis, the equipment comprising an electrochemical planar sensor, a measuring cell and means for adjustment of hydrodynamic conditions within the measuring system.

Background of the Invention

Electro-chemical analysis is a very effective analytic tool, as output signals are in a form of electric voltage or current. Application of microelectronic technologies results in a significant decrease of costs of electrodes, their miniaturisation and improvement of their utility properties. By all types of electrodes response, measurement accuracy and ruggedness of a construction significantly depends upon a flow of an electrolyte with analysed sample in a vicinity of the applied electrode. To ensure defined hydrodynamics in the electrode vicinity there can be used an electromagnetic stirrer. The stirrer located in the electrolyte flow provides for improved coating of the electrode working surface by the electrolyte. Nevertheless the arrangement features a significant increase of undesired output signal noise which is due to a turbulent circulation in the electrode vicinity. The defined hydrodynamic flow in the electrode vicinity could be achieved by amending a profile of a channel around the electrode. Such an arrangement allows for sedimentation of chemicals at the beginning or end the profile. Another drawback of such a solution is present by equipment with multiple measuring electrodes, where it is necessary to design a complicated structure of the distribution channel. Such a construction is costly and the equipment is liable to failures.

Another known systems for defining hydrodynamic conditions within the measuring equipment utilise thin-layer flowing applying means called thin-layer sensors, described e.g. in the paper "Electro-analytic measurements in flowing liquids" by Štulík and Pacáková, published in 1989. In this system there are used substantially three basic electrode designs. By the first type the cell is designed as a U-shaped tube with the working electrode in the

middle. By the second type, described in literature as "wall-jet", the cell is constructed as a T-shaped tube. A sample enters the cell through the central beam and the working electrode is located opposite the central beam mouth into the transverse beam through which the sample flows out of the cell in both directions. The third type is called a "tubular" cell, with the working electrode located in a tube which the sample flows through. All these detectors are well known and work satisfactory if only one working electrode is used. By multiple working electrodes there appear problems with even distribution of the liquid sample to individual electrodes. In a case of a serial arrangement of the working electrodes there comes another problem as the electrodes located further down the sample flow are influenced by products or reactions occurring at the electrodes located ahead of them.

The "wall-jet" system was later extended to two electrodes in a "ring-disk" arrangement, as described in a papers „New Electro-analytical Techniques Applied to Medicine and Biology" and „Electrochemical detectors, Fundamental Aspects and Analytical Applications" published by Alerby and Haggett in 1984. There is also known a construction with an electrode surrounded by means for improvement of hydrodynamics in the electrode vicinity. Such an arrangement has been described by Horword and Chichester in their paper "Instrumental Methods in Electrochemistry", published in 1985. Practical embodiments comprise industrial flowage measuring cells with forced turbulence. In the measuring cell there are located bars, a fluid bed, filling bed and where appropriate, there may be used also a cylindrical electrode, rotating co-axially with the cell. It is a drawback of all these constructions that their application to systems with multiple detecting elements is very difficult.

The best results as far as defined hydrodynamics and transfer of mass towards an electrode are concerned have been reached with disc electrodes. A rotating electrode of this type consists of a flat disc having a diameter of 1 up to 3 mm, the disc being located at end of a non-conducting rod, which is rotating very fast while submerged in a solution. The solution is stirred by the rotating disc. Thus the problem of diffusion is limited only to a transport of

particles through non-moving solution layer, sticking to the electrode surface. As long as the rotation speed is constant and effect of stirring is repeatable, than all experiment utilising rotating disc electrodes are performed under same conditions. Rotating disc electrodes manifest several advantages when compared with rigid electrodes. Among them there has to be mentioned the known theory of the electrode hydrodynamics allowing for mathematical processing of measured data with accuracy and correctness comparable with a mercury bead electrode. In comparison with other rigid electrodes the rotating disc electrode active surface can be re-established with better reproducibility by electrochemical process. Due to defined and reproducible stirring this electrode shows also higher sensitivity than it is by classic rigid electrodes while the problem of diffusion is restricted only to non-moving layer on the electrode surface. On the other hand the rotating disc electrodes have also some disadvantages such as lower measurement reproducibility, rather difficult transfer of a signal having a value of nA units from the rotating part of the measurement equipment onto a static part of the equipment, very complicated design of the electrode structure and resulting high investment costs. Among other disadvantages there should be mentioned a complicated exchange of one sensor for another one and the fact that residues of analysed sample remain in the equipment thus preventing to apply flow analysis.

It is an object of the invention to eliminate above described drawbacks of present solutions, improve hydrodynamics of the system and enable to define adjustment of the distribution body with respect to measuring electrodes.

Disclosure of the Invention

The foregoing object is achieved by an equipment for chemical analysis comprising an electrochemical planar sensor, a measuring cell and means for adjustment of conditions of hydrodynamics within the measuring system designed in accordance with the present invention, the said equipment comprising the electrochemical planar sensor forming an integral part of at

least a bottom and/or cover of the measuring cell and the means for adjustment of conditions of hydrodynamics within the measuring system having a distribution body which is revolvingly seated and engages with means for its rotation. The equipment may work either in a flow mode or in an inside circulation mode. Further in accordance with the present invention the measuring cell bottom is detachable, thus allowing for an easy exchange of sensors. In a preferred embodiment both the distribution body and the means for its rotation are placed on an arm, which is adjustable along a line perpendicular to a plane of the planar sensor. Still further in accordance with the invention the distribution body is provided with a shaft having at least one longitudinally arranged channel for flow of analysed sample, the channel opening into the measuring cell. In a preferred embodiment the channel is arranged parallel to the shaft. The analysed sample may be transported into the measuring cell even through the planar sensor, which in such a case has to be furnished with provided with at least one opening for entry of the sample into the measuring cell. For the flow mode operation the measuring cell is furnished with an outlet for outflow of the analysed sample. By the embodiment for the inside circulation mode the shaft is preferably provided with at least one radially arranged passage, which is interconnected with the channel. Better performance is achieved when the measuring cell is provided with a disc shaped screen arranged plan-parallel with the distribution body and extending like a ring around the shaft. Further improvement is achieved when a surface of the distribution body facing the planar sensor is provided with projections and/or grooves and/or is coarsened.

The equipment for chemical analysis designed in accordance with the invention provides for optimisation of measuring system hydrodynamics. It also allows for accurate adjustment of the distribution body with respect to electrodes of the planar sensor. The equipment may be operated either in a flow mode or in a mode with an inner circulation of a measured sample.

Brief Description of the Drawings

By way of examples the invention will be now described with reference to the accompanying drawing. Fig. 1 presents the said equipment in a front fragmentary vertical cross-section and Fig. 2 shows a cross-sectional view taken along lines A-A in Fig. 1. Fig. 3 offers a front fragmentary vertical cross-section of a measuring cell with a planar sensor in a form of the cell cover. Fig. 4 illustrates a vertical cross-sectional view of a measuring cell with a planar sensor the in a form of a cover, where rotation of the distribution body is derived from a rotating disc carrying electromagnets. Fig. 6 depicts the arrangement with inner sample circulation and Fig. shows a preferred embodiment for the arrangement according to Fig. 6.

Description of Preferred Embodiments

Referring to Fig. 1, there is shown an equipment for chemical analysis comprising a measuring cell 1, planar sensor 2 and a stand with means for adjustment of hydrodynamics of the measuring system. The measuring cell 1, planar sensor 2 and the stand are located on a base 3. The stand, spaced apart from the measuring cell 1, consists of a column 4 and an arm 5. The arm 5 is arranged perpendicularly to the column 4 and is vertically adjustable on the column 4. At one end of the arm 5 there is rotateably seated a vertically arranged shaft 6, while at the other arm 5 end there is mounted an electric motor 7 having its rotor axis vertically arranged. The shaft 6 is at its lower end furnished with a distribution body 8 having a shape of a disc. The shaft 6 is also provided with a central co-axially arranged channel 9, which at the lower end opens on a bottom surface of the distribution body 8, while at its upper end is adapted for connection to the inlet of an analysed sample. The shaft 6 engages with the motor 7 by means of a belt 10 and pulleys 11, the pulleys seating at the shaft 6 and the driving pin of the motor 7. The distribution body 8 together with above described means for its rotation and the arrangement for adjustment of the vertical position of the arm 5 constitute means for adjustment of hydrodynamics of the measuring system.

In the working position the shaft 6 with the distribution body 8 extends into the measuring cell 1. The vertical position of the distribution body 8 within the measuring cell 1 is set manually, by shifting the arm 5 along the column 4. The arm 5 is connected with a pivot 12 which is slidingly seated in the column 4 axis and is connected with co-axially arranged motion screw 13. The motion screw 13 revolves in a nut 14 attached to the column 4. Any clearance between the screw 13 threads is eliminated by a wound spring 15, which is positioned at the motion screw 13. The adjustment of a desired position of the distribution body 8 is facilitated by an indicator 16 engaging by means of the motion screw 13 with the pivot 12.

The measuring cell 1 being of a tubular shape has a detachable bottom, which is sealed to the cell tubular wall by means of an O-ring 17. In the cell bottom there is located the planar sensor 2 having at least one electrode. The tubular wall of the measuring cell 1 is provided with two fixtures 18, allowing for a set-up and fixing of the measuring cell 1 by adjustment screws 19 with wing nuts 20. By fastening the wing nuts 20 the O-ring 17 is compressed and the cell casing with the cell bottom makes the measuring cell 1 a hermetically closed unit. An inlet 21 in the cell tubular wall allows for drainage of the sample out of the measuring cell 1.

A liquid comprising a measured sample enters the measuring cell 1 through the channel 9, which is at its upper free end supported by a holder 22 attached to the arm 5. By rotation of the distribution body 8 the sample is evenly spread over working electrodes of the planar sensor 2.

The described embodiment enables accurate adjustment of a position of the distribution body 8 above the electrodes and makes optimization of the measuring system hydrodynamics feasible.

Another arrangement of the measuring cell 1 and the planar sensor 2 is presented on Fig. 3. The electrochemical planar sensor 2 is an integral part of a cover 23 of the measuring cell 1. The cover is again sealed by the O-ring 17. The distribution body 8 rotation is induced by moment magnetic transfer from magnets 24 located on the pulley 11 engaging by means of belt 10 with electric motor. The electric motor is not depicted on the Fig. 3.

The liquid containing a sample is supplied through a central channel 9, rigidly attached to the measuring cell 1 body, The channel 9 opens into the measuring cell 1 co-axially with the axis of rotation of the distribution body 8. The sample output 21 is located in the measuring cell 1 tubular wall.

Another embodiment applying the flow measuring cell 1 of the thin-layer type is presented in Fig. 4. Liquid carrying a sample enters the measuring cell 1 in axis of rotation of the distribution body 8, thus being equally distributed to individual electrodes of the planar sensor, and leaves radially through the outlet 21. Moment of rotation is brought from the disc 25 furnished with magnets 24, the disc 25 rotating within the space above the planar sensor 2, which makes the cover 23 of the measuring cell 1. The inside space of the measuring cell 1 is sealed by means of the O-ring 14. The arrangement of this embodiment of the invention is suitable for simple applications where measurement accuracy is not so important, as here magnetic lines of force run through connections of the electrodes and induce noise voltage. This drawback is eliminated by the embodiment illustrated in Fig. 5. The measuring cell 1 operates similarly as by the preceding design. Unlike the above design here the sample enters the measuring cell 1 through opening 26 in the planar sensor 2. Rotation of the distribution body 8 is forced by rotation of magnets 24 placed on a disc 25, which is located under the planar sensor 2. Therefore the magnetic lines of force do not cross connections of the electrodes and induction of noise voltage is significantly reduced.

The above described solution can be applied also for analysis carried out in a non-flow mode, by analysis of a given amount of a sample, by so called batch-analysis. For such a mode the shaft 6 is provided with at least one radial passage 27, which is connected with the channel 9. This arrangement allows for a circulation of the sample, as the liquid comprising the sample is from the outlet 21 area returned through the passage 27 to the channel 9 and to the measuring electrodes of the planar sensor 2 at the bottom of the measuring cell 1. To eliminate circulation of the sample in the vicinity of input into the distribution body 8, the measuring cell 1 may be preferably equipped with a screen 8, which during rotation of the distribution body 8 remains

stationary. The screen 28 has a shape of a disc arranged plan-parallelly with and above the distribution body 8 and in a shape of a ring encircling the free lower part of the shaft 6 extends further up to the mouth of the passage 27 into the channel 9.

To increase effectiveness of the equipment, especially for analysis of liquids showing high viscosity, the face of the distribution body 8, i.e. its surface facing the planar sensor 2, may be provided with projections and/or grooves and/or is coarsened.

CLAIMS

1. Equipment for chemical analysis comprising an electrochemical planar sensor, a measuring cell and means for adjustment of conditions of hydrodynamics within the measuring system, **characterised in,** that the electrochemical planar sensor (2) makes an integral part of at least a bottom and/or cover (22) of the measuring cell and the means for adjustment of conditions of hydrodynamics within the measuring system comprise a distribution body (8) which is rotateably seated and engages with means for its rotation.

2. Equipment for chemical analysis according to claim 1, **characterised in,** that the measuring cell (1) bottom is detachable.

3. Equipment for chemical analysis according to claim 1 or 2, **characterised in,** that the measuring cell (1) is furnished with an outlet (21) for outflow of the analysed sample.

4. Equipment for chemical analysis according to any of the preceding claims, **characterised in,** that both the distribution body (8) and means for its rotation are placed on an arm (5), which is adjustable along a line perpendicular to a plane of the planar sensor (2).

5. Equipment for chemical analysis according to claim 1 or 2, **characterised in,** that the distribution body (8) is provided with a shaft (6) having at least one longitudinally arranged channel (9) for flow of analysed sample, the channel (9) opening into the measuring cell (1).

6. Equipment for chemical analysis according to claim 5, **characterised in,** that the channel (9) is arranged parallel to the shaft (6).

7. Equipment for chemical analysis according to claim 5 or 6, **characterised in,** that the shaft is provided with at least one radially arranged passage (26) interconnected with the channel (9)

8. Equipment for chemical analysis according to any of the claims 1 up to 4, **characterised in,** that the planar sensor (2) is provided with at least one opening (25) for entry of the analysed sample into the measuring cell (1).

9. Equipment for chemical analysis according to any of the preceding claims, **characterised in,** that a surface of the distribution body (8) facing the planar sensor (2) is provided with projections and/or grooves and/or is coarsened.

10. Equipment for chemical analysis according to claim 7, **characterised in,** that the measuring cell (1) is provided with a screen (27) shaped as a disc arranged plan-parallel with the distribution body and extending like a ring around the shaft (6).

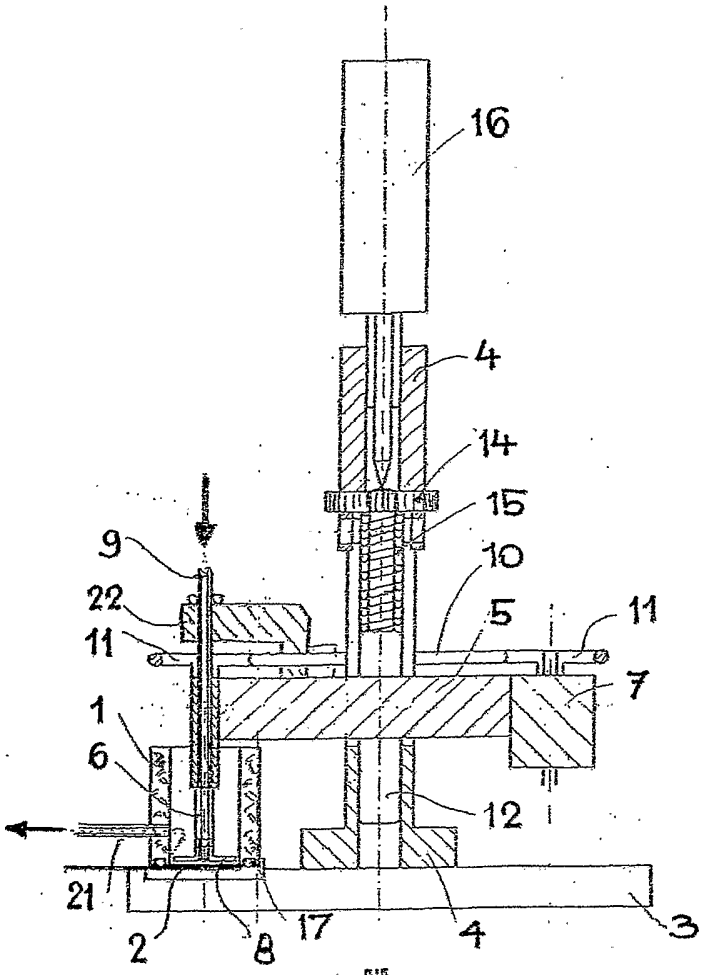
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Fig. 1

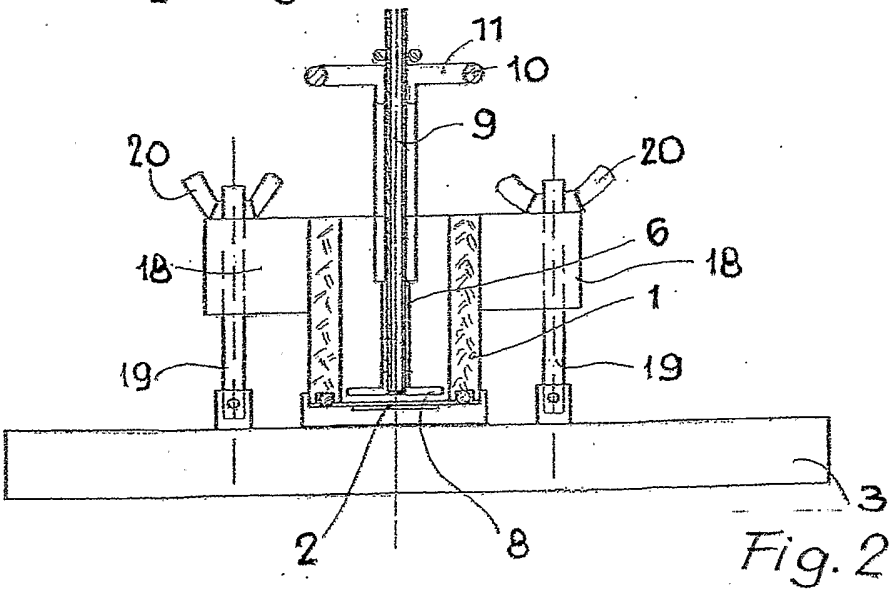
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Fig. 2

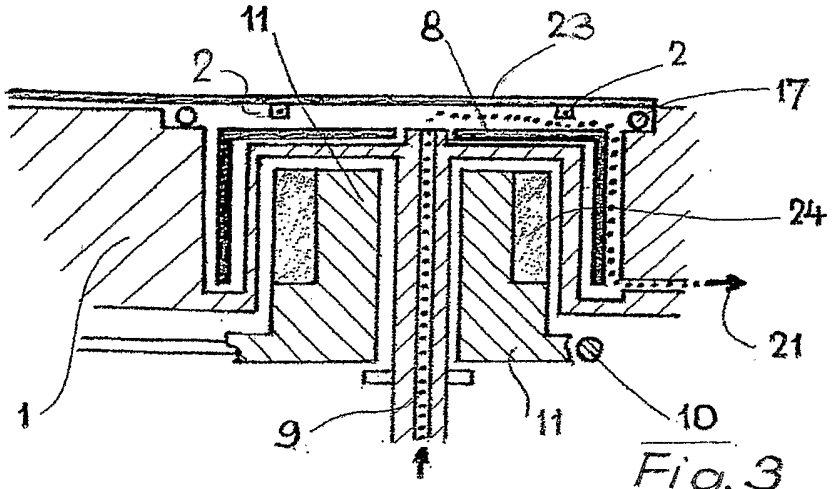

Fig. 3

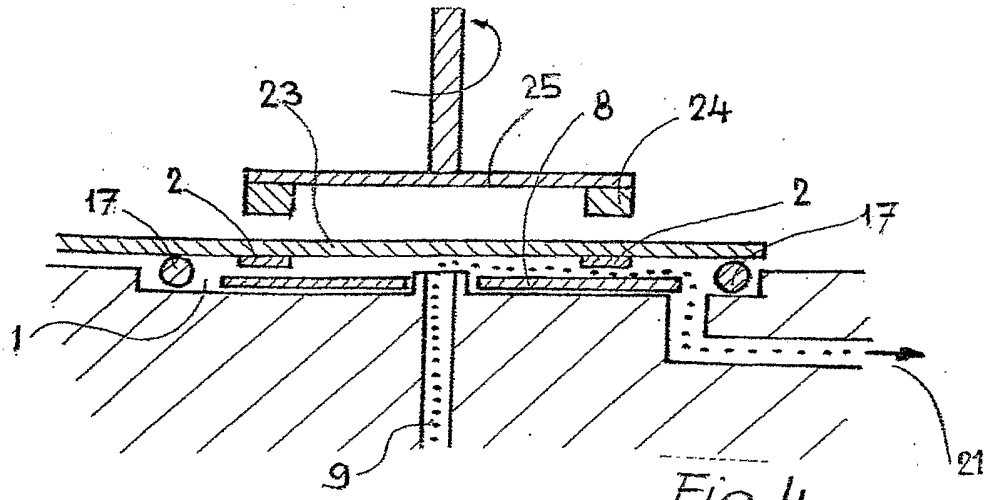

Fig. 4

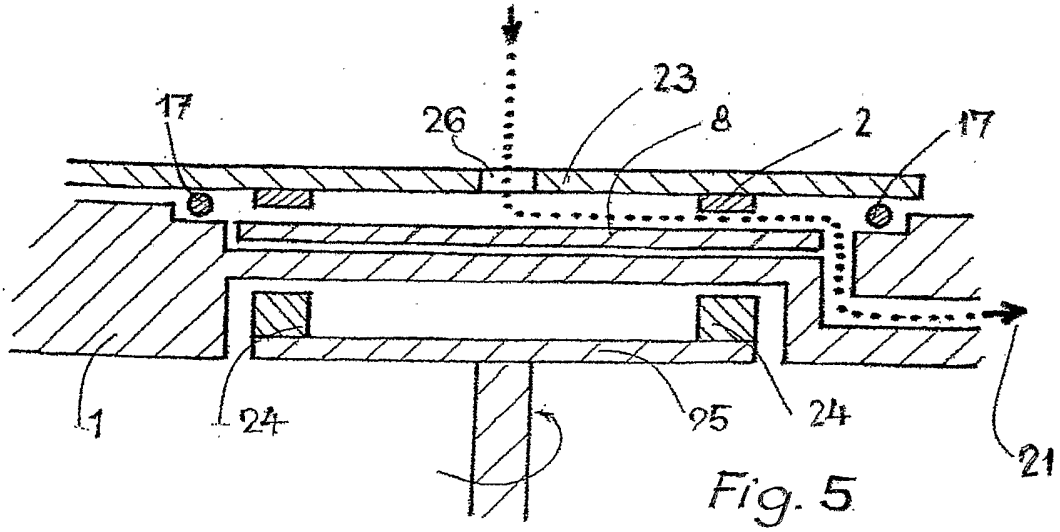

Fig. 5

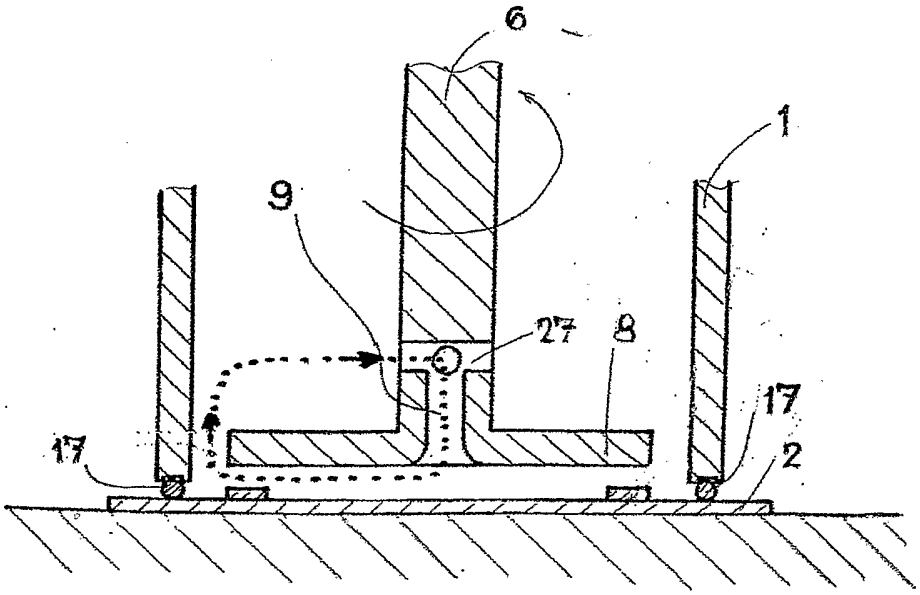

Fig. 6

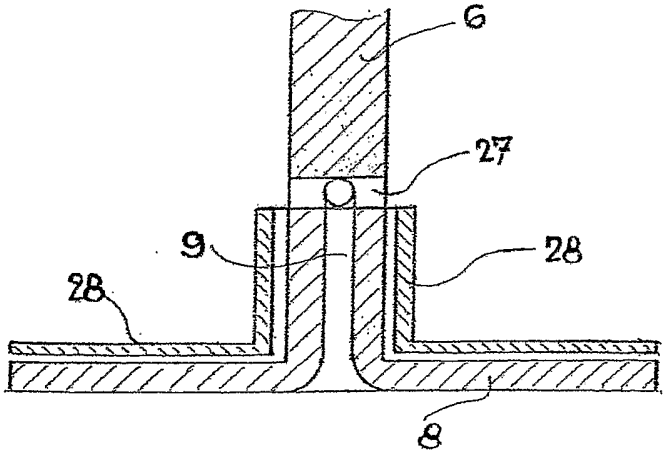

Fig. 7

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CZ 03/00063

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G01N27/416 G01N27/49

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 3 498 888 A (JOHANSSON GILLIS RUNE) 3 March 1970 (1970-03-03) column 4, line 64 -column 5, line 75; figure 1	1-4,9 5-8
A	CZ 287 676 B (KREJCI ENGINEERING ING) 17 January 2001 (2001-01-17) the whole document	1-10
Y	GB 2 028 870 A (EFFLUENT TREATMENT LTD) 12 March 1980 (1980-03-12) page 2, line 37 - line 55; figure 1	5-8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
5 March 2004	22/03/2004

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/CZ 03/00063

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