



EXPERTS IN WATER CHEMISTRY SINCE 1903



9072 Hydrazine Analyzer User Manual



WALTRON CUSTOMER COMMITMENT

This instruction manual is a technical guide to aid the customer in the set-up, operation, and maintenance of their new Waltron measuring system. Waltron provides continuous product improvement and reserves the right to make any modifications to the information contained herein without notice.

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Technical questions concerning this product should be addressed to:

Waltron Technical Service Department

Flemington, New Jersey

Phone: (908)-534-5100

Fax: (908)-534-5546

www.waltron.net

Please be ready to provide the following information:

- Date analyzer was purchased
- Analyzer model and serial number
- Recent maintenance history
- Calibration slope values and detailed description of problem

Waltron's technical expertise and extensive experience provides personalized solutions to the water quality industry. It is Waltron's commitment to provide the customer with timely and accurate technical service and support.

Waltron fully expects the customer to be satisfied with the quality, performance, and cost of this product.

If there are any questions or concerns regarding this product, please feel free to contact Waltron at (908)-534-5100.

Thank you for choosing Waltron!

Please note the Waltron mailing and shipping address:

Waltron Bull & Roberts, LLC
25 Minneakoning Road, Suite 101
Flemington, NJ 08822



SAFETY

Please observe proper safety and handling precautions when installing, operating, maintaining, and servicing this product. The following should be noted and adhered to:

- Read and understand manual before working with analyzer.
- Pay special attention to warning labels on enclosures, containers, packages and chemicals.
- Only qualified personnel should be involved in the installation, operation, and servicing of the analyzer.
- Follow safety precautions when operating analyzer in conditions of high pressure and/or temperature.
- Keep analyzer chemicals away from heat and extreme temperatures. Reagent powders must be kept dry.
- Follow all regulations and warning labels when disposing of chemicals. Do not mix chemicals.

To obtain analyzer safety information or Safety Data Sheets (SDS), please contact Waltron or logon to www.waltron.net.



WARRANTY AGREEMENT

If, within one year from the date of shipment, the customer experiences any equipment defects or is not satisfied with the analyzer manufacturing, Waltron will repair, or at its option, replace any defective part(s) free of charge. This warranty requires that the defective part(s) be returned to Waltron with shipping charges prepaid.

At Waltron discretion, a Technical Service Specialist may be sent out to repair or replace the defective part(s) on location. Traveling time and expenses of the Technical Service Specialist is at the customer's expense.

Equipment sent to Waltron must be appropriately packaged and the following information must be provided prior to returning to Waltron:

- The Return Authorization (RA) number assigned to the customer by the Waltron Technical Service Department
- Customer name, address and department
- Name and telephone number of the individual responsible for returning items for repair
- Brief problem description

Ship to Waltron service center:

Waltron Bull & Roberts, LLC
25 Minneakoning Road, Suite 101
Flemington, NJ 08822

The Waltron Warranty Agreement:

- Covers expendable sensors for one month after shipment and reusable electrodes for six months after shipment.
- Does not apply to damages occurred during shipping.
- Warranty will be nullified if goods have been used for purposes other than those for which they are intended or if any seal has been removed, broken or tampered with or if the Waltron trademark or serial number has been removed, defaced, or altered.
- Does not cover expendable supply items such as reagents, tubing and electrolytes.
- Does not cover misuse or mistreatment by the user.
- Does not cover previous repair or alteration by unauthorized individuals.

Waltron does not assume responsibility for contingent liability through alleged failure or failures of products or product accessories.



CHECKLIST OF MATERIALS

- In order to ensure customer satisfaction, Waltron does its best to provide adequate and timely packaging and shipping services. Please perform the following after receiving a shipment:
- Inspect all shipping containers upon receipt and record any visible damage. If there are any outward signs of damage, please retain all containers and packages for inspection by carrier. Please retain all packing material so that it can be used for future moving and shipping needs.
- Check all items received against those on the packing list. Chemicals are usually shipped in a separate package and will be itemized accordingly.
- Verify that the number of packages received agrees with the packing list and shipping papers.
- Notify both Waltron and the carrier if any problems occur.

Important Notice:

- All analyzers are inspected and tested prior to shipment.
- In normal use, the unit should require only minor maintenance and should operate correctly and without fault over a long period of time.
- Please note that if electronic components need to be replaced, it may be necessary to adjust and/or calibrate the analyzer.
- Failure to carry out correct maintenance procedures may result in inaccurate analyzer readings.



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1 INTRODUCTION

1.1 AREAS OF APPLICATION

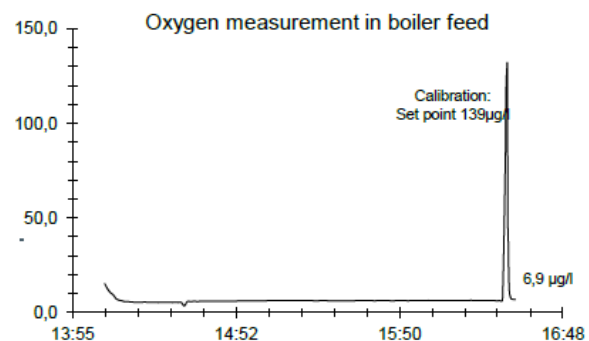
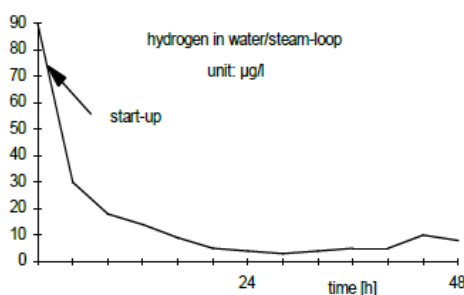
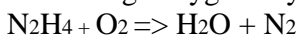
The Waltron 9072 Hydrazine Analyzer is used for the automatic, continuous measurement and control of hydrazine concentration in aqueous solutions. Examples of the applications of the unit include the determination of residual hydrazine concentration in boiler feedwater in power plants, the monitoring of hydrazine concentration in the primary loop of a nuclear power plant, the monitoring of hydrazine concentration during, or the indication of the hydrazine concentration during the reduction of oxygen in water treatment plants etc.

Hydrazine is used as a reducing agent and oxygen scavenger in fossil fueled boiler systems, generally in AVT (All Volatile Treatment) process streams. The hydrazine creates a reducing environment to protect copper containing metallurgy and serves to reduce the dissolved oxygen concentrations to protect iron containing metallurgy.

Hydrazine concentration needs to be continuously monitored to provide feedback to the chemical injection systems and to ensure that the correct concentrations are present in the system.

In the primary loop of a nuclear power plant the hydrazine should reduce or mitigate the oxygen which is produced by radiolysis. As a result the electro-chemical corrosion potential (ECP) of the tube material is reduced. In nuclear power plant applications, hydrazine is added to scavenge oxygen or recombine with the oxygen that is produced by radiolysis. In the pressurized water reactor (PWR) primary loop, hydrazine is measured in the range 25-50cc/kg. Hydrazine in boiling water reactors (BWR) feedwater and reactor coolant is measured in ppm's. Hydrazine in feedwater is typically 0-2ppm and hydrazine in reactor coolant water will vary between 0.1-0.5ppm.

For boilers that operate with a pressure higher than 62 bar (900 psi), hydrazine is often dosed to scavenge oxygen. Hydrazine (N₂H₄) reacts with oxygen as follows:



1.2 DESCRIPTION OF DEVICE

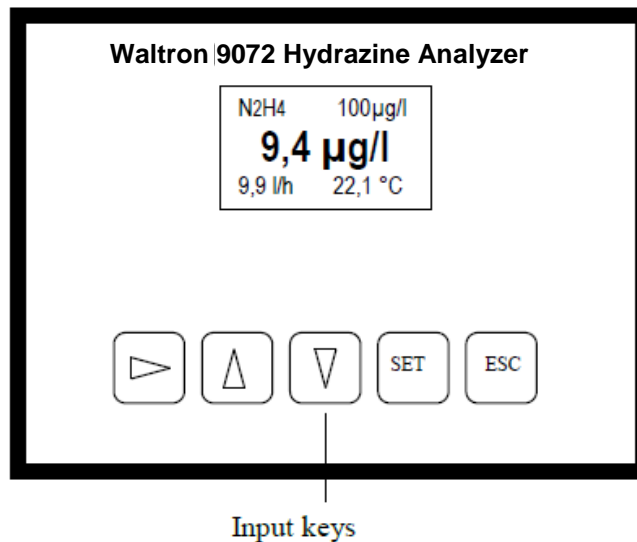
The Waltron 9072 Hydrazine Analyzer measures reliably and quickly the hydrazine concentration in aqueous media from the trace areas ($<10.0 \mu\text{g/l}$) up to concentrations of higher than $1000 \mu\text{g/l}$ under normal conditions.

The Waltron 9072 Hydrazine Analyzer can be divided into two primary function parts. The first is the electronic component which consists of the display and input elements as well as the measuring data collection and data processing elements.

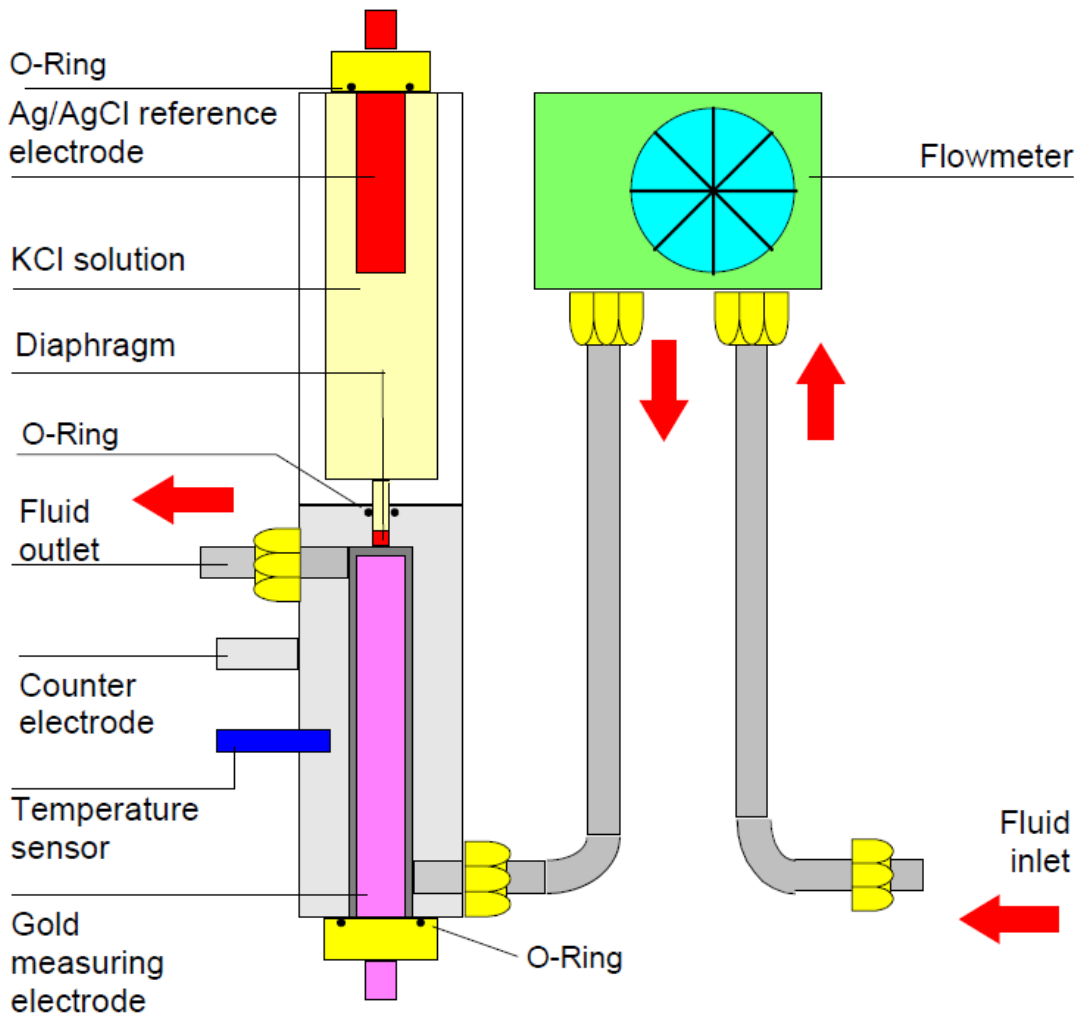
The second is the analytical component which is composed of the inlet valve, filter device and flow meter which serve the sample and probe preparation. The measuring cell is joined with the temperature sensor and the reference cell with its reference electrode.

For the measurement of the hydrazine (N_2H_4), the sample flows through the components of the device which relate to the sample and probe preparation and through the calibration cell into the coaxial measurement cell (grooved measurement cell), passing by the gold measuring electrode. If the measuring electrode has the characteristic potential for the hydrazine oxidation in the boundary layer (interphase) between the electrode surface and medium, the measurement reaction takes place.

Front view

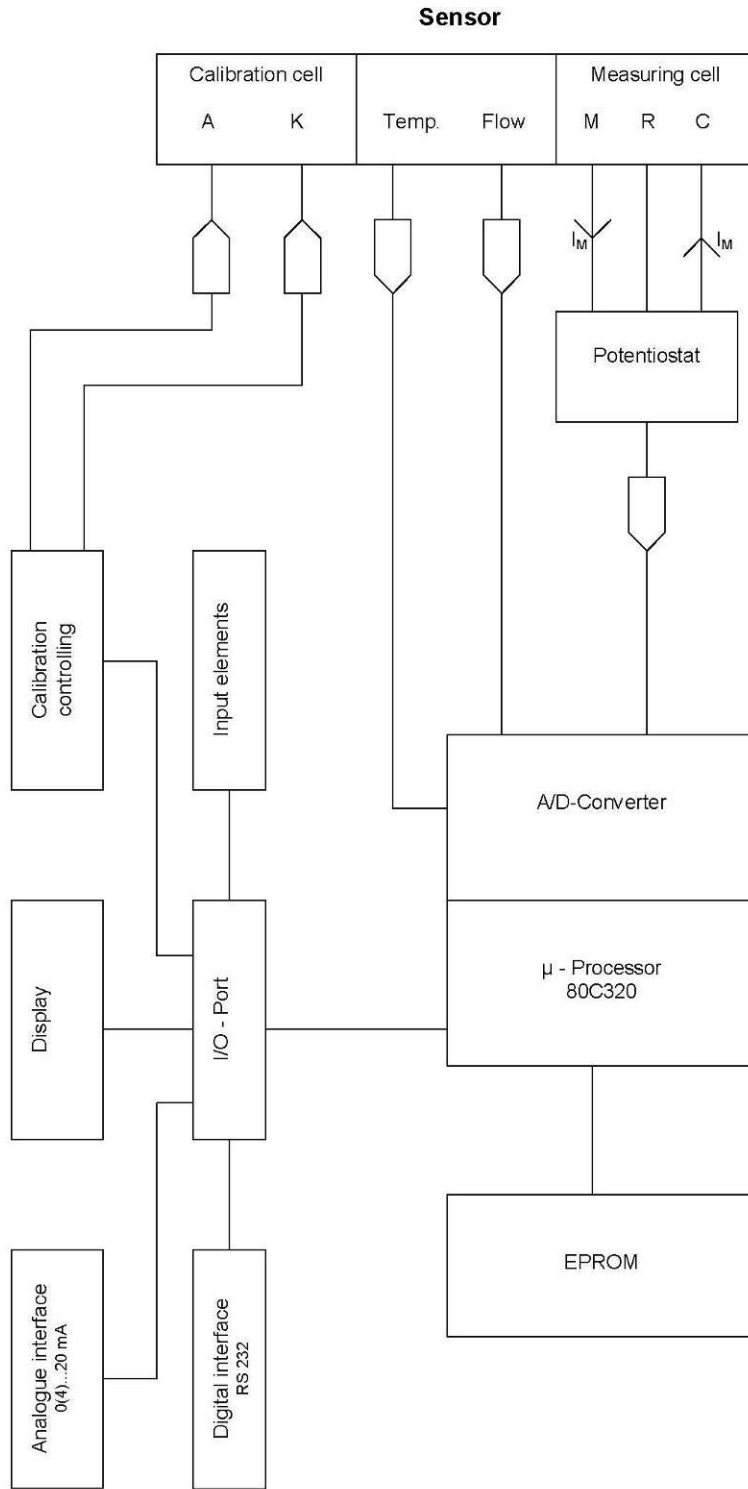


1.3 THE MEASURING SYSTEM



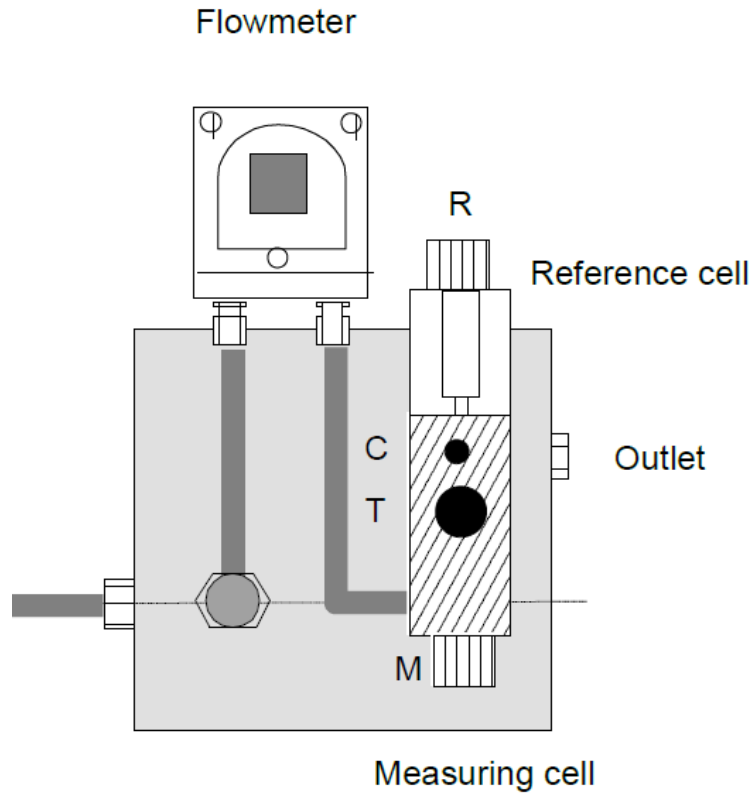
Measuring cell

1.4 BLOCK DIAGRAM OF SENSOR SYSTEM



2 INSTALLATION

2.1 *DELIVERED PARTS*



Arrangement of the wall mounted instrument

M: measuring electrode

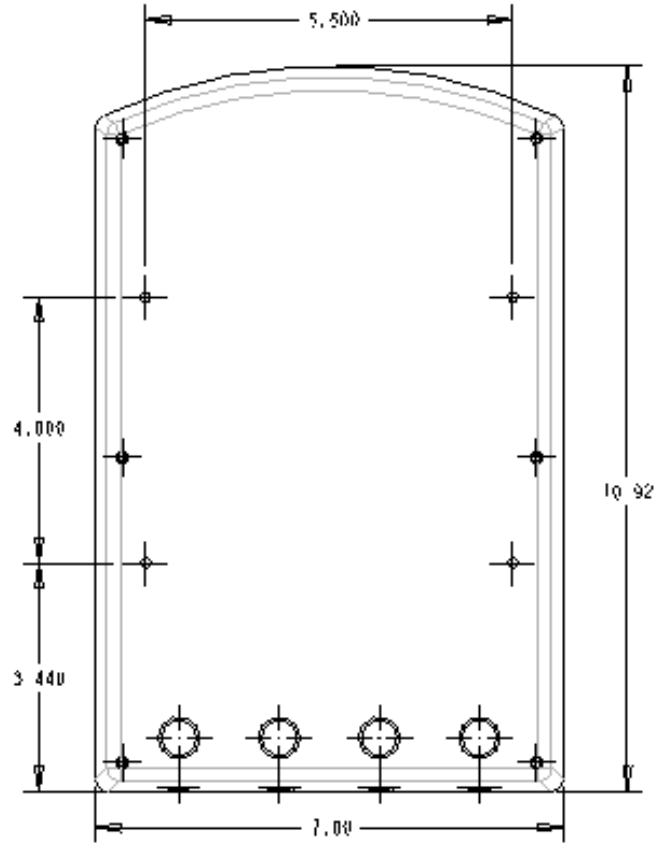
C: counter electrode

R: reference electrode

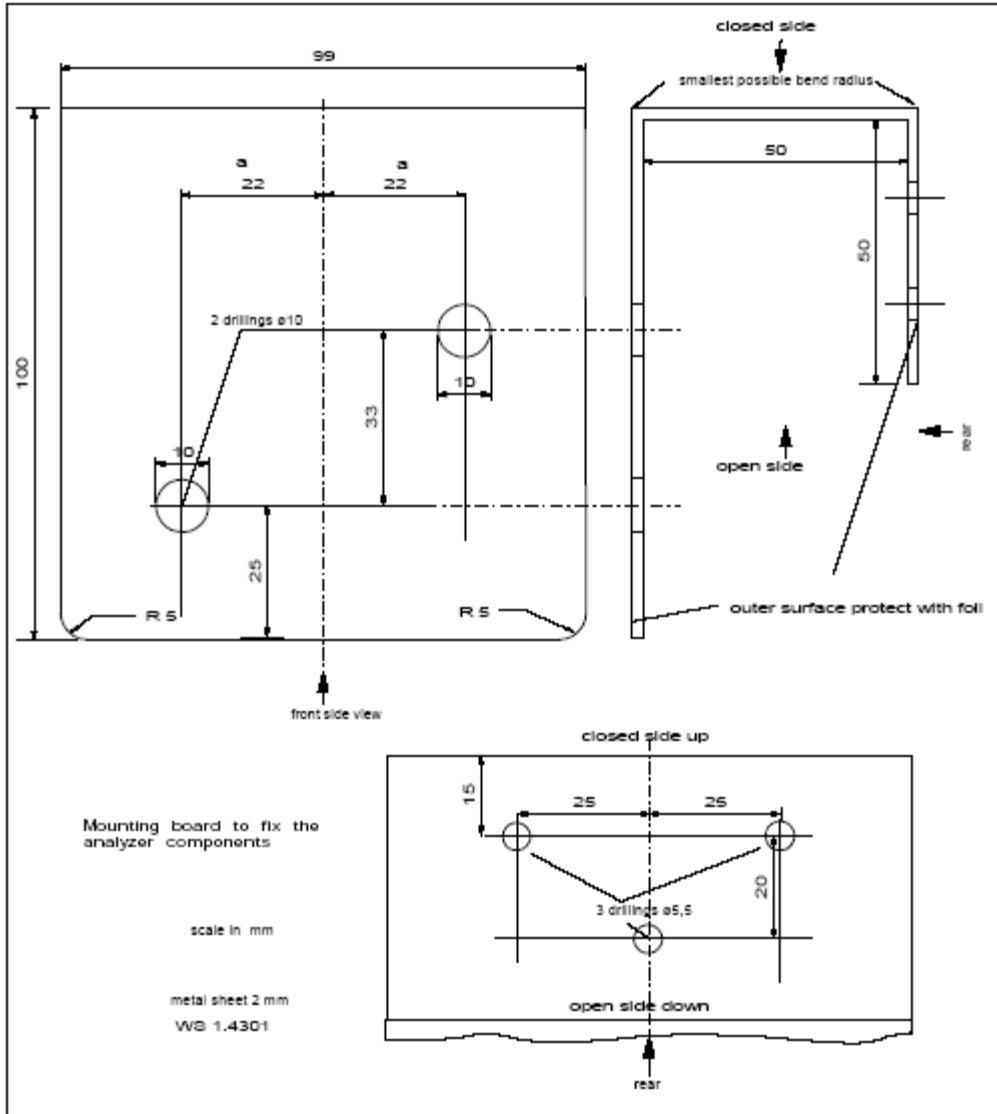
T: temperature sensor



TRANSMITTER MOUNTING



WET SECTION MOUNTING





2.2 ACCESSORIES

1. 100 ml KCl-solution
2. 1 kg granular marble
3. 1 test tube brush
4. 1 cleaning material
5. 1 software for digital measuring (option)

2.3 TERMINAL SCHEMATIC

Terminal Block Left:

L	N	PE	1	2	3	4	5	6	7	8	9
Line 100-230 V 50/60 Hz	Line 100-230 V 50/60 Hz	Ground (earth)	Limit alarm (off)	Limit alarm (on)	Limit alarm (common)	Alarm on	Alarm off	Alarm (common)	Auto changing range 2	Auto changing range 1	Auto changing (common)

Terminal Block Right:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
0(4)..20 mA -	0(4)..20 mA +	Cal. electrode + (A)	Cal. electrode -(K)	Flow (signal)	Flow	Flow +	Temp.sensor (common)	Temp.sensor (common)	Temp.sensor +	NC	Reference el. (R)	Counter el. (C)	Measure el. (M)	NC	TxD (RS 232)	GRD (RS 232)	RxD (RS 232)

2.4 TECHNICAL DATA

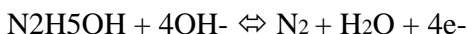
Measurement principle:.....	microprocessor based, potentiostatic three electrode system
Calibration:.....	build-in, single button operation
Auto-calibration:.....	option
Measuring range:	
Measuring group I:.....	0,0.....1000,0 μ g/l range selectable between 20....1000 μ g/l
Measuring group II:.....	0,00.....10,00 mg/l range selectable between 0.2....10 mg/l
Auto-changing-range:.....	Built in
Analog output:.....	0(4).....20 mA; shunt max. 500 Ohm
Digital output:.....	serial interface RS 232
Data logging:.....	Ring time buffer 21,000 data points, time set 1 s to 5 min
Limit:.....	power relay
Alarming:.....	power relay; Flow and Calibration
Measuring electrode:.....	gold
Counter electrode:.....	stainless steel 1.4571 (314)
Reference Electrode:.....	Ag/AgCl in saturated KCl-solution
Calibration electrode:.....	None
Response time t_{90} :.....	8 sec
Probe conductivity:.....	$\geq 3 \mu$ S/cm; (if conductivity is less a salt cell is required)
Ambient temperature:.....	0....+55 °C
Sample temperature:.....	0....+60 °C, automatic compensation
Sample pressure:.....	≤ 8 bar (116 psi)
Sample flow:.....	3 l/h20 l/h
Sample fittings:.....	tube fittings for tube \varnothing 6 mm
Error limits:.....	< 1 % in range 1000,0 μ g/l, or $\pm 2\%$ in range 100,0 μ g/l
Protection class:.....	IP 65
Color:.....	basic parts RAL 7035; front and rear parts RAL 7024
Voltage:.....	100...240 VAC, 50/60 Hz
Power consumption:.....	10 VA



3 OPERATING PROCEDURES

3.1 PRINCIPLE OF MEASUREMENT

The 9072 Hydrazine Analyzer electrochemical hydrazine sensor functions in a potentiostatic mode with an open three-electrode system. The measuring electrode is made of solid titanium, coated with gold. The counter electrode is made of stainless steel and the reference electrode is made of silver/silver-chloride. The use of open measuring electrode means, that there is a direct contact between the sample and the measuring electrode. A membrane is not required. For the measurement of dissolved hydrazine (N₂H₄) the fluid medium flows into the coaxial measurement cell between the platinum measuring electrode and counter electrode. If the measuring electrode has reached the correct potential, hydrazine is oxidized in the interphase boundary layer. The electrochemical reaction may be represented qualitatively as:



The characteristic potential for this reaction the potential at which hydrazine oxidation occurs in preference to other competing reactions is measured by holding the potential of the measuring electrode steady with a potentiostatic and comparing its value with that of the reference electrode. Under these conditions the rate of the electrochemical reaction is limited by the rate of diffusion of hydrazine molecules to the electrode. As long as we remain within this 'diffusion-limiting-current' area, the electrochemical cell delivers an electric current, whose size depends linearly on the concentration of dissolved hydrazine. This current, which is measured by the instrument's electronic processing unit, is known as the diffusion-limiting current,

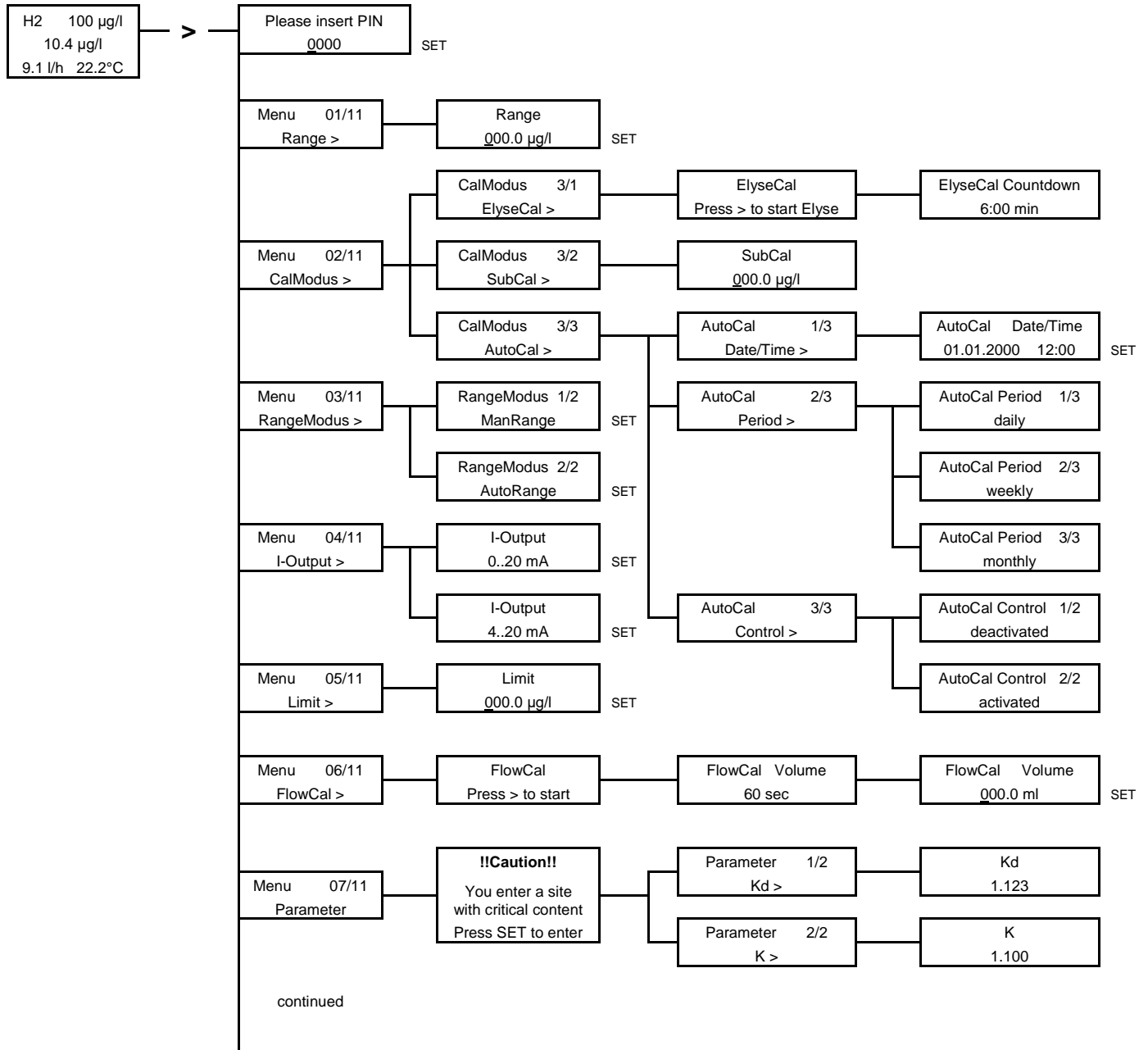
$$I_{\text{diff}} \cdot c_{\text{N}_2\text{H}_4} = k \cdot I_{\text{diff}}$$

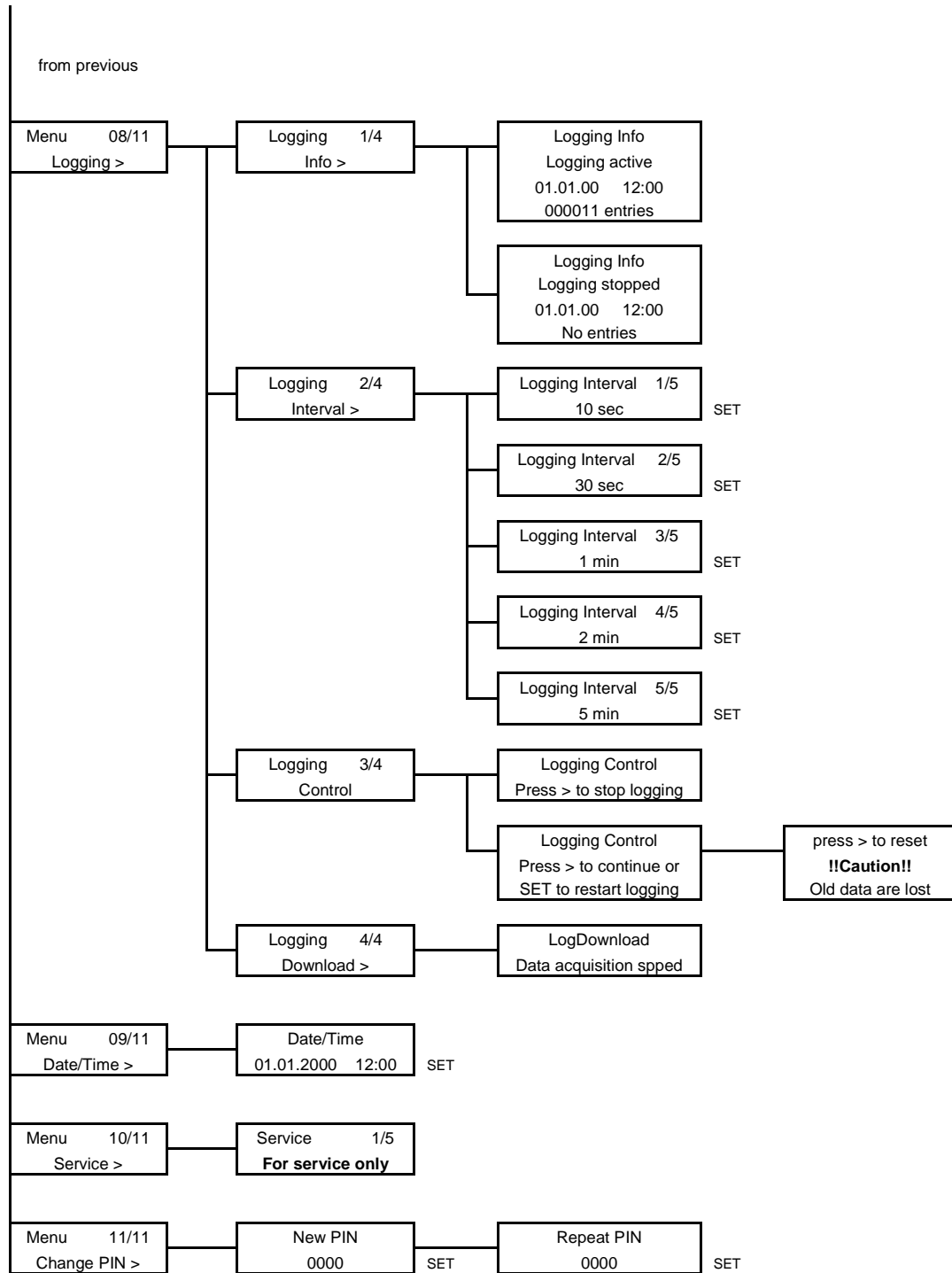
This diffusion-limiting current depends mainly on the mass transport of the electrochemically active components, and hence on the hydrodynamics in the measuring cell. It therefore changes significantly with the temperature and flowrate through the measuring cell. In practice the flowrate and temperature vary over wide ranges, but the instrument corrects these changes by using empirical correlations.

A second important influence on the measurement is the condition of the electrodes. In particular the adsorptive and oxidative state of the electrode surface layers. This is independent of the flow conditions; it depends instead on the voltage between the electrode and the electrolyte, and on the material of which the electrode is made. Appearing flow- and temperature effects of the measuring signal are recorded with the aid of the installed flow meter and temperature sensor and are compensated, if necessary.

4 START-UP

4.1 MENU STRUCTURE





4.2 PREPARING TO MEASURE

Before you start to measure you must perform the following procedures:

1. The electrical power supply has to be connected according to the local power authority guidelines with the terminal box, with which the connectors to the 0(4)...20 mA analog output (see the circuit diagram on the cover plate) should be combined.
2. The reference cell has to be filled with KCl solution. The reference cell must be removed from the measuring cell by unscrewing the reference cell. Take out the reference electrode and fill up the KCl solution to the level of about the beginning of the external threading. Make sure that no air bubbles develop near the diaphragm. Tap the cell gently if necessary. Remove any surplus of the KCl solution and reinsert the reference electrode. Make sure that the installation of the O-ring is correct.
3. If the sample has a conductivity of $\leq 3 \mu\text{S}/\text{cm}$, the salt cell (option) must be filled with granular marble (calcium carbonate CaCO_3). To do this unscrew the cover and pour in the granular marble carefully into the large cavity.
4. The probe tube is connected with tube fittings to the inlet valve. The outlet line is placed at the measuring cell exit with a hose having a 5 mm inside diameter.

4.3 CHOICE OF OPERATING PARAMETERS

Before starting measurement, set your operating parameters. With the keys at the front site you can move through the menu. To enter the menu, press key \triangleright and insert your code number (**Pre setting: 0000; see page 17**). With the keys ∇ and Δ you move one step in the vertical direction up or down and also increase or decrease numbers. With the key SET you confirm chosen parameters, with the key ESC you jump back one step in the horizontal direction with **no effect**.

If a > sign is displayed, you can go with the key \triangleright right ahead in a sub-level.

The menu consists of eleven levels. You find your present position on the right top of the display.

1st Menu level *Range* > shows range settings. The value is corresponding to the maximum analog output current of 20 mA. Press key \triangleright and make your choice by setting digit for digit and press the adjacent key SET. Your range is now selected and the indication jumps one step back in the *Menu*.

2nd Menu level shows the calibration settings named *CalModus* >. Press key \triangleright to jump to the sub-level *CalModus* > which consists of three sub-levels called: *ElyseCal* >, *SubCal* > and *AutoCal* >. (**option only**). With the key \triangleright you can go ahead. With the key \triangleright you will release the electrolytic calibration if you start from position *ElyseCal* >. From



SubCal > you are setting the present hydrazine concentration digit for digit, finally push key SET.

3rd *Menu level Range Modus* > gives you the choice between *ManRange* (range which is setting in 1st level only) and *AutoRange* (automatic changing range which has double value of *ManRange* >)(Option only).

4th *Menu level I-Output* > sets the analog output current 0(4)...20 mA.

5th *Menu level Limit* > allows limit settings. There exists a switch hysteresis of 10% of the chosen limit.

6th *Menu level FlowCal* > enables flow meter calibration (see *Section 7*).

7th *Menu level Parameter* > shows operation parameters Kd (flow) and k (calibration).

Attention: Only reading parameter.

8th *Menu level Logging* > is the data logging function (Option only).

9th *Menu level Date/Time* > allows date settings.

10th *Menu level Service* > **is for service only.**

11th *Menu level ChangePIN* > gives you the possibility to change your PIN number.

Attention: lost PIN numbers can only activated by the manufacturer.

5 MEASURING MODE

5.1 OPERATING CONDITIONS

For an accurate measurement of hydrazine, the probe's environment must fulfill certain conditions regarding conductivity, flow, temperature and pressure.

- The sample conductivity must be $\geq 3 \mu\text{S}/\text{cm}$; otherwise the salt cell must be refilled (see also *Section 4.2*).
- The flowrate has to be between 3 l/h and 208 l/h (The optimal flowrate is about 10 l/h).
- The temperature of the sample should range between 1 °C and 60 °C.
- The pressure to which the probe should be subjected at least 400 mbar and may not exceed 8 bar. Operating conditions outside this range require either a probe pump or a pressure reducing valve.

Connect the probe line on the fitting tube of the inlet valve. Adjust the flow very carefully and slowly. You have to make sure that no sudden pressure occurs and you should verify that all air bubbles in the tube system rinse out. To help the bubbles to rinse out, open and close quickly the inlet valve several times.

Attention: Make sure that the plugs stay dry.

5.2 ANALYZER CALIBRATION

After the hydrazine analyzer is installed and the medium flows through the analyzer, the calibration can be performed. The first calibration should take place after letting the sample flow, for approximately 30 minutes. During the calibration the operation conditions should not change.

Method 1: by a parallel chemical determination of the hydrazine concentration (classical laboratory method)

You are in the mode for hydrazine measurement and have pressed key \square and insert your PIN number. Select SubCal:

SubCal 000.0 $\mu\text{g}/\text{l}$
--

The setting of the present hydrazine concentration is performed digit for digit. If the value is correct, press key SET. Your calibration value is stored and the instrument determine the current sensitivity of the measuring electrode by the modern microprocessor. The indication jumps one step back in the menu. The k-Factor value can be displayed in the level Parameter > k-Factor.

Method 2: Prepare a solution with a defined hydrazine concentration in 5 liter canisters.

Example: Approach of the dilution series

a) Starting solution 24% hydrazine hydroxide ($\text{H}_2\text{H}_5\text{OH}$) = 15% N_2H_4 = 150 g/ l N_2H_4

b) **Solution A:** Add 10 ml starting to 1000 ml deionized water = 15 g/ l N_2H_4

b) **Solution B:** Add 10 ml **solution A** to 1000 ml deionized water = 150 g/ l N_2H_4

Calibration solution: Add 16.7 ml of **solution B** to 5 l hydrazine-free water = 500 μg / l N_2H_4

You start the calibration procedure by pressing key \blacktriangleright and insert your PIN number.

Select SubCal:

SubCal 000.0 μg /l

The setting of the present hydrazine concentration is performed digit for digit. To reach the measuring mode, press the key ESC twice.

If the value is beneath 10 % of the value determined through the calibration, which followed after a cleaning procedure, a new cleaning of the electrode is necessary.

6 MAINTENANCE

6.1 *CLEANING OF ELECTRODES*

Reference electrode: The surface of the reference electrode is made of silver chloride (AgCl), by a galvanic process, and must not be cleaned.

Measuring electrode: The measuring electrode has to be cleaned (activated) if the sensitivity (k-Factor) of the measuring electrode is beneath 10 % of the determined value, calculated after that calibration, which followed a cleaning. As discussed above, the k-Factor can be looked up in the menu Parameter > in the 7th level.

Before you remove the measuring electrode, it is necessary to empty the analyzer (of sample). Then remove the plug (M) from the measuring electrode and unscrew the thrust screw of the electrode. Take the electrode slowly out of the cell. You should be careful not to drop the measuring electrode and not to hit it against the cell wall. Clean the surface with a mild detergent, by rubbing gently the electrode between your middle finger, index finger and thumb. During the cleaning, do not press too hard the electrode. This procedure should not last longer than 2 minutes (the Pt-layer is only several μ m thick). Rinse well with water and do not touch the surface of the electrode with your fingers thereafter.

Occasionally a wiping of the electrode surface with a clean tissue is sufficient. Thereby you reduce the later start up time until steady state condition.

6.2 *CLEANING OF CELLS*

The cleaning cycle of both the counter electrodes of the measuring and calibration cells is the same as those of the measuring electrode and calibration electrode. To clean the counter electrodes, you close the inlet valve and remove the plug connectors (A), (K) for the calibration cell, as well as (M), (C) and (R) for the measuring cell. Disconnect the pipe between the calibration cell and the flowmeter. Disassemble the calibration cell from the square mounting by detaching the fitting (screw width SW 12 mm). Remove the calibration electrode (see also the instruction for cleaning electrodes above). Clean the interior with a mild detergent and a thin test tube brush (see also "Spare parts"). Examine, if the nozzle in the top part (diameter \varnothing 0.8 mm) is free. After the cleaning you have to rinse the cell well with water. The dismantling of the measuring cell from the square mounting should be performed in the same way as the calibration cell. Remove the outlet pipe and unscrew the reference cell from the measuring cell (see also *Section 4.2*). Take the electrode slowly out of the cell (see also *Section 6.1*). The cleaning procedure thereafter is the same, as described for the calibration cell.

When reassembling, make sure that all parts are dry.



7 TROUBLESHOOTING

- If the values of the flow measurements seem incorrect, a calibration of the flow meter should be performed. The procedure has to be as follows:
 1. Adjust the flow to approximately 10 l/h and have available a 250 ml graduated cylinder.
 2. Choose the *FlowCal* > level and press the key ▷ and follow the displayed instructions.
 3. If the countdown runs beginning at 60 sec collect the flow during the 60 second period in the graduated cylinder. When the countdown is completed, stop collecting the flow.
 4. The amount (in ml) of sample, collected in the cylinder during the 60 seconds, should be entered digit by digit with the keys Δ, ▽, and ▷. If the value is correct, press key SET. Press key ESC to go back to the measuring mode.
- If you observe unsteady or unlikely results during the measurements, check if the plug connectors are dry and make sure that the reference electrode is completely immersed into the KCl-solution.
- During longer periods, where no measurement takes place, (for example longer than 3 weeks) it is advisable to clean the analyzer. There should not remain any probe material or KCl solution within the analyzer. In case of shorter breaks, parts can stay in wet surrounding. It will reduce the start up time and the time until steady state condition.



8 SPARE PARTS AND ACCESSORIES

1 Set of O-rings (TA).....	L1000-001
100 ml of KCl-solution.....	L1000-002
1 kg of granular marble.....	L1000-003
1 Reference electrode.....	L1000-004
1 Measuring electrode (Au/N ₂ H ₄).....	L1000-005
1 Test tube brush.....	L1000-006
1 Stck. reference cell.....	L1000-007
1 Stck. cleaning material.....	L1000-008
1 Measuring electrode (Ag/O ₂).....	L1000-009
1 Measuring electrode (Pt/H ₂).....	L1000-010
1 Salting cell (TA).....	L1000-011
1 Salting cell (TI).....	L1000-012
1 Sieve.....	L1000-013
1 Set of O-rings (TI).....	L1000-014
1 Flow meter (TA).....	L1000-015
1 Flow meter (TI).....	L1000-016
1 Electrode Holder.....	L1000-017
1 Temperature Sensor.....	L1000-018
1 Cable Bundle.....	L1000-019
1 Calibration.....	L1000-020
1 Measuring Cell (High Range).....	L1000-021
1 Calibration.....	L1000-022
1 Measuring Electrode (Pt/H ₂ , high).....	L1000-023
1 Measuring Cell (Low Range).....	L1000-024
1 Temperature Safety Valve, type TPS 371.....	L1000-025
1 Microfilter, type FF50, Complete.....	L1000-026

TA parts for wall mounted instrument

TI parts for portable instrument