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A Comparative Study of the Electrode Systems of Three pH and Blood Gas Apparatus

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Summary: We present a comparative evaluation of the electrode systems of three modern blood gas analysers: IL-413, ABL-1 and AVL-937C.

The response curves, accuracy and precision of the pH-, pCO₂- and pO₂-electrodes were established with tonometered blood and buffer solutions.

pH values (range 6.8—7.8) measured on the AVL deviate (-0.03 pH for blood and +0.03 pH for buffer) from those of BMS2 Mk2; whereas on the IL and ABL analysers the pH values deviate by not more than 0.01 pH. The standard deviation was better than 0.005 pH.

pCO₂ values of blood and buffer (range 14–106 mm Hg) deviate from the calculated tonometer values by quantities ranging from 3 to 10 mm Hg. The average precision $(\overline{CV})^1$) of the pCO₂ measurement on each analyser was better than 1.8%.

pO₂ values of blood (range 0-130 mm Hg) did not differ by more than 3 mm Hg from the calculated values. Above 130 mm Hg a linear negative increasing difference was seen.

For buffer solutions a linear relationship between pO_2 difference and pO_2 value was found over the whole range from zero up to 642 mm Hg: a positive difference below and a negative difference above the pO_2 of the previous calibration; if the calibration pO_2 is higher, the sample pO_2 is shifted to a higher value.

The average precision of the pO₂ measurements was better than 3%. In the (patho)-physiological range the three instruments may provide suitable results for the clinician. Suggestions are made for standardization and improvement of the electrode systems.

Vergleichende Untersuchung der Elektrodensysteme von drei pH- und Blutgas-Meßgeräten

Zusammenfassung: Eine vergleichende Bewertung der Elektrodensysteme von drei modernen Blutgasanalysatoren (II-413, ABL-1, AVL-937C) wird vorgestellt.

Ansprechbarkeit, Richtigkeit und Zuverlässigkeit der pH-, pCO₂- und pO₂-Elektroden wurden mit tonometriertem Blut und Pufferlösungen festgestellt.

Die am AVL gemessenen pH-Werte (Bereich 6,8-7,8) weichen für Blut um — 0,03 und für Puffer um + 0,03 von den mit dem BMS2 Mk2 gemessenen ab, während sie am IL und ABL nicht mehr als 0,01 pH abweichen. Die Standardabweichung war besser als 0,005 pH.

pCO₂-Werte von Blut und Puffer (Bereich 14-106 mm Hg) weichen von den berechneten Tonometer-Werten um 3 bis zu 10 mm Hg ab. Der Mittelwert der Genauigkeit (VK) der pCO₂-Messung an jedem Gerät war besser als 1,8%.

pO₂-Werte von Blut (Bereich 0-130 mmHg) differierten um nicht mehr als 3 mm Hg von den berechneten Werten. Oberhalb 130 mm Hg wurde eine lineare, negativ steigende Differenz beobachtet.

¹⁾ CV: average coefficient of variation.

Für Pufferlösungen wurde eine lineare Beziehung zwischen pO_2 -Differenz und pO_2 -Wert über den gesamten Bereich von 0 bis 642 mm Hg gefunden: eine positive Differenz unterhalb und eine negative oberhalb des pO_2 des letzten Kalibriergases; wenn das pO_2 des Kalibriergases höher ist, weicht der pO_2 -Wert der Probe zu einem höheren Wert hin ab und umgekehrt.

Der Mittelwert der Genauigkeit (\overline{VK}) für die pO₂-Messungen war besser als 3%. Im (patho)-physiologischen Bereich können die drei Instrumente dem Kliniker ausreichende Ergebnisse vermitteln. Vorschläge für die Standardisierung und Verbesserung der Elektrodensysteme werden gemacht.

Introduction

The importance of providing an accurate, precise and rapid blood gas analysis has been recognized by physicians in clinical disciplines, such as pulmonology, cardiology, thoracic surgery, intensive care, resuscitation and anaesthesiology. The pH, pCO₂ and pO₂ determination of blood often gives essential information for the diagnosis and care of patients whose life is at risk.

Initially the measurements of pH, pCO₂ and pO₂ were made separately and the whole procedure was laborious. The increase in the number of demands for blood gas analysis from the clinic has, however, stimulated several manufacturers to develop more sophisticated, fast and automatic blood gas systems, designed for simultaneous measurement of pH, pCO₂ and pO₂.

Sources of error associated with pH and blood gas measurement are well described (1-8) and reviewed (9-11). If the sources of error are not carefully under control, the risk of an analytical bias is great as demonstrated by Miller & Tutt (12) who compared blood gas instruments of four manufacturers. Hill & Tilsley (13) found systematic deviations from the stated values using tonometered blood samples. Similar observations were made by others (14-16).

We were stimulated by these facts to compare and evaluate the operation of the electrode systems of three modern blood gas analysers, namely the IL (Instrumentation Laboratories Inc., Lexington, Mass., U.S.A.) Model-413, the ABL Radiometer, Copenhagen, Denmark) Model-1, and the AVL (AVL AG, Schaffhausen, Switzerland) Model-937C. The response, accuracy and precision of the electrode systems were tested with both tonometered blood (17) and buffer solution AIII²) (18). The latter may be applied for quality control (19). For reference pH measurements, the BMS2 (Radiometer, Copenhagen, Denmark) Model Mk2 was used.

Materials and Methods

Apparatus

Table 1 shows important features and specifications of the different instruments as given by the manufacturers.

Design

The cells for pH measurement consist of a glass electrode and a reference electrode which is connected with the sample by an open salt bridge in the ABL and by a salt bridge with a permeable membrane in the IL and AVL; the KCl concentration in the bridges is different.

The principle of the pCO₂ electrode is based on pH measurement in a bicarbonate layer which is embedded in a nylon matrix in ABL and IL, and in a piece of cellophane in the AVL. The layer is separated from the sample by a teflon membrane in the ABL and AVL and by an Ilastic membrane, which is more permeable to carbon dioxide, in the IL. The electrode sensitivity ($S = -dpH/dlog\ pCO_2$) of IL and ABL is approximately 0.95, and of AVL below 0.90 as a result of the buffering effect of the cellophane.

The pO₂ electrode is a polagraphic cell consisting of a platinum cathode and a silver/silver chloride anode, immersed in an electrolyte solution and covered with a membrane of propylene in the IL and ABL and of teflon in the AVL. The cathode of the AVL electrode consists of more threads of platinum.

Procedure

The operations of calibration, sampling, reading and rinsing are different on the three instruments and are described in more detail below.

TL-413

A complete calibration for pH, pCO_2 and pO_2 electrodes can be done by alternate selection of two push buttons: cal 1 and cal 2.

Calibration 1 is done with phosphate buffer pH = 7.384 and a gas mixture (low gas) composed of carbon dioxide and air.

Calibration 2 is done with a phosphate buffer pH = 6.840 and a gas mixture (high gas) composed of carbon dioxide and nitrogen (tab. 1).

In our set-up the gas-mixtures for calibration were delivered by a pair of gas mixing pumps (type A27/2F. Wösthoff, Bochum, Germany).

Before sampling the pH electrode and the gas electrodes are exposed to the conditions of cal 1.

Two push buttons are used for sampling. By pressing the "tip" button the sample path is cleared and the sampling tip presented. By pressing the "sample" button the aspiration of the sample is initiated. This operation can be performed automatically or manually.

Separate "ready" indications light up according to the preset limits (see tab. 1) for each electrode. When all three electrode signals indicate "ready", a "data" indication light appears. The instrument memory stores the values for pH, pCO_2 and pO_2 at time "data" for computation.

The working cycle is finished with a rinsing and a calibration step (cal 1). Rinsing of the sample path is performed in a direction opposite to sampling, to prevent obstruction of the sample path by blood-clots.

ABL-1

Calibration, sampling, reading and rinsing are fully automated and controlled by a computer. Every two hours the three electrodes are calibrated with two gas equilibrated phosphate buffer solutions (tab. 1). Calibration of $pO_2 = 0$ mm Hg is performed electrically.

²⁾ See material and methods.

Tab. 1. Specifications of the pH, pCO₂ and pO₂ electrode systems.

		IL-413	ABL-1	AVL-937C
pH	glass electrode	capillary type	flat membrane	flat membrane
	liquid junction	cellophane	open	cellulose acetate
		4.3 mol/l KCl	3.0 mol/l KCl	1.0 mol/l KCl
pCO ₂	membrane	ILastic	teflon	teflon
	thickness	100 μm	12 μm	15 μm
	spacer	nylon	nylon	cellophane
	eloctrolyte	100 mmol/l NaCl 20 mmol/l NaHCO ₃	20 mmol/l NaCl 5 mmol/l NaHCO ₃	25 mmol/l KCl l mmol/l NaHCO ₃
pO_2	membrane	polypropylene?	polypropylene	teflon
	thickness		20 μm	25 μm
	cathode, diameter	25 μm	20-25 μm	$50 \mu m$ (4 threads of 12.5 μm)
	polarizing voltage	700 mV	630 mV	700 mV
	electrolyte	10 mmol/l KH ₂ PO ₄	470 mmol/l phosphate buffer	153 mmol/l NaCl
		10 mmol/l K ₂ HPO ₄	pH 7	
		100 mmol/l KCl	134 mmol/l KCl saturated	
			with Ag Cl	
General	gas mixing device	external	internal	internal
	Calibration	Cal 1	"green" calibrating solution	gas 1
	(B = 760 mm Hg)	pH 7.384	pH 6.841	pCO ₂ 35 mm Hg
		(1:3.5 NBS*) phosphate, IL)		pO ₂ 140 mm Hg
		pCO ₂ 35 mm Hg	pCO ₂ 82 mm Hg	gas 2 (not humidified)
		pO ₂ 140 mm Hg	pO ₂ 132 mm Hg	pCO ₂ 70 mm Hg
		Cal 2	"red" calibrating solution	gas 3 (not humidified)
		pH 6.840	pH 7.383	pO ₂ 0 mm Hg (pure CO ₂)
		(1:1 NBS phosphate, IL)		buffer 1 pH 7.383
		pCO ₂ 70 mm Hg	pCO ₂ 41 mm Hg	(1:4 Sörensen phosphate AVL
		pO ₂ 0 mm Hg	pO ₂ not measured	buffer 2 pH 6.840
				(1:1 NBS, phosphate, AVL)
	measuring mode	manual and automatic	automatic	manual
	sample volume	350 μl; 100 μl (micro)	< 500 μl	40–60 μl
	rinsing solution	11 mmol/l NaCl and 8 mmol/l	saline	distilled water
		NaHCO ₃ bubbled with low gas		
	electrode preset	pH < 0.02 pH/min		pH < 0.012 pH/min
	limits	$pCO_2 \le 2.0 \text{ mm Hg/min}$	print-out after 120 s	$pCO_2 \le 1.2 \text{ mm Hg/min}$
		$pO_2 \leq 2.0 \text{ mm Hg/min}$		pO ₂ < 1.2 mm Hg/min
	electrode "ready" indications	one for each electrode	none	only one for three electrodes
	simultaneously	one	three	one
	visible	~		
	read outs			

^{*)} NBS: National Bureau of Standards

Values for pH, pCO₂ and pO₂ are printed after a fixed period of 120 s. Subsequently the rinsing cycle is initiated in the opposite direction. When the instrument is in "ready" position the cuvette is filled with humidified calibration gas 1, which is replenished at 10 min intervals.

AVL-937C

The instrument is equipped with a commutator (sliding selector) with six operational positions: G1, G2, G3, M, W and S. The calibration of the pH electrode and the gas electrodes is performed separately. Gas calibration is done using successively gas 1 (low pCO₂ in air), gas 2 (high pCO₂ in air) and gas 3 (pure carbon dioxide). Only gas 1 is humidified and thermostated (tab. 1). pH calibration has to be done by filling the capillary measuring chamber in the position M, with the two phosphate buffers successively. The sample is introduced in the same position.

One "ready" indication light is used in succession for the three measuring channels. We decided however to read the pO_2 value after 30 s and the pCO_2 and pH after 2 min because the adjustment of the preset limits was not adequate as shown by the response curves of the electrodes (see results). Calibration adjustments were done at the same points of time.

When the commutator is in the position "wash-dry" the chamber is washed by intermittent suction of distilled water and air and dried by suction of air for twenty seconds.

Gases

Gases of known pCO₂ and pO₂ for tonometry were obtained by means of gas mixing pumps (type M-200, mixing range 1-99%, type A27/2F, mixing range 1-10% and A 18/2F, mixing range of 10-90%; Wösthoff, Bochum, Germany). The desired mixtures were made from pure carbon dioxide, nitrogen, oxygen and

air, dried before use and mixed at the same pressure. The percentages of carbon dioxide and oxygen in the mixtures were verified by means of gas analysis with the *Haldane-Lloyd* apparatus (Gallenkamp, London). The relative accuracy of these gas mixtures was better than 1%.

Samples

Blood

Fresh venous blood, drawn from volunteers or patients into heparinized collecting tubes, was used. To obtain blood samples with extremely low or high pH values isotonic solutions of NaCl with appropriate quantities of NaHCO₃ or HCl were added (20).

Buffer AIII

Solutions were prepared, based on the composition of the NBS equimolal phosphate buffer, and 30 mmol NaHCO₃ and 30 mmol NaCl per liter were added (18).

Tonometry

Aliquots of 3 to 4 ml blood or buffer AIII were equilibrated in a Laué tonometer (Eschweiler and Co., Kiel, Germany) with a pre-humidified gas mixture for at least 30 minutes. Both tonometer and humidifier were submerged in a water bath, maintained at 37° C; fifteen different gas mixtures were employed; six containing carbon dioxide (2-15%) in air and nine containing oxygen (0-90%), carbon dioxide (10%) and nitrogen to 100% by volume.

Procedure

Tonometered samples were carefully drawn from the tonometer with a 1 ml disposable polystyrene syringe, flushed previously with tonometer gas. The samples were measured immediately according to the manufacturer's instructions with the exception of the above mentioned modifications of the reading time for AVL. Only one parameter (pH, pCO₂ or pO₂) was evaluated simultaneously on the three instruments.

The procedure for estimation of electrode response curves was as follows:

IL-413. After introduction of a tonometered sample in the "automatic" mode this knob was switched to "manual" and a stopwatch was started immediately.

During three minutes the electrode signal was read every 15 s from the digital screen.

ABL-1. During a measuring period of 120 s the first up-dating for each parameter appeared after 30 s and the subsequent up-datings at 18 s intervals.

AVL-937C. Immediately after sampling, a stopwatch was started and the electrode signals registered every 15 s for three minutes.

The reference pH determinations were performed on the BMS2, calibrated with precision phosphate buffers (type S1500, pH = 6.841 and type S1510, pH = 7.383; Radiometer). Samples were aspirated in the electrode capillary three times without intermittent flushing and drying. For a comparison with the pH value obtained from the other instruments, the mean pH of the second and the third reading was used.

Calculation

The partial gas pressure of carbon dioxide or oxygen in a gas mixture of known composition was expressed in mm Hg, and calculated by multiplying the barometric pressure (B) minus the pressure of water vapor (47 mm Hg at 37°C), by the volume fraction of the respective gas.

Conversion of pCO_2 and pO_2 values into values at 760 mm Hg is done by multiplying measured or calculated values by the factor (760-47)/(B-47).

The pH-log pCO₂ relationship of buffer solution AIII was computed according to Veefkind et al (18).

Results

pН

Response curves

Figure 1 shows the response curves of the pH electrodes for tonometered blood and buffer samples in the pH range 6.9-7.6.

The pH values between time "ready" and "data" for IL, and between the first updating and "print-out" for ABL do not differ by more than 0.005 of a pH unit, because drift is less than 0.002 of a pH unit/min within 30 s.

On the AVL we found a drift of 0.010-0.015 of a pH unit/min during 3 min, although the green light usually indicated pH "ready" within 30 s. Further investigations revealed a large drift at low pH coupled with high pCO₂, and at high pH coupled with both low and high pCO₂. This indicates that drift is caused on the one hand by leakage of carbon dioxide at the electrode edges, and on the other hand by a slow response of the electrode at more alkaline pH. We have chosen a reading time at 120 s for the AVL, because at that time the drift is smaller in the higher pH range, and the calibration buffer has reached a plateau value.

Accuracy

The accuracy of the pH determination was established by comparing pH values from IL, ABL or AVL with those from the BMS2 for blood (fig. 2) and buffer (fig. 3).

The estimated pH differences scattered within 0.015 of a pH unit for blood samples at each pH level for all three instruments, which was probably the result of the diversity of the blood samples. The figures illustrate a good agreement for IL and ABL up to pH 7.5; pH values are comparable with BMS2 values within 0.01 of a pH unit. Above pH 7.5 the pH differences of the IL values deviate while those of ABL remain constant.

The different behaviour of the electrodes could be explained by the different glasses used for their construction. As previously demonstrated (3) the efficiency factor of a glass electrode determined with two phosphate buffers over the pH range 6.8—7.4 might be too high for the range pH > 7.4. This effect is dependent on the kind of glass. The results with the ABL and BMS2 pH electrodes, which are manufactured from the same kind of glass, deviate from those obtained with the IL electrode, which is constructed from Ingold glass.

pH values for blood and buffer samples measured on the AVL deviate by about 0.03 of a pH unit from the BMS2 pH values. The opposite direction of these deviations: positive for buffer and negative for blood, is most peculiar. The large deviation for buffer could be explained partly by a pH difference of —0.015 of a pH unit of the calibration buffer "7.383"; we found a pH of 7.368 instead of 7.383 for three different batches of AVL phosphate buffer measured on the BMS2. The

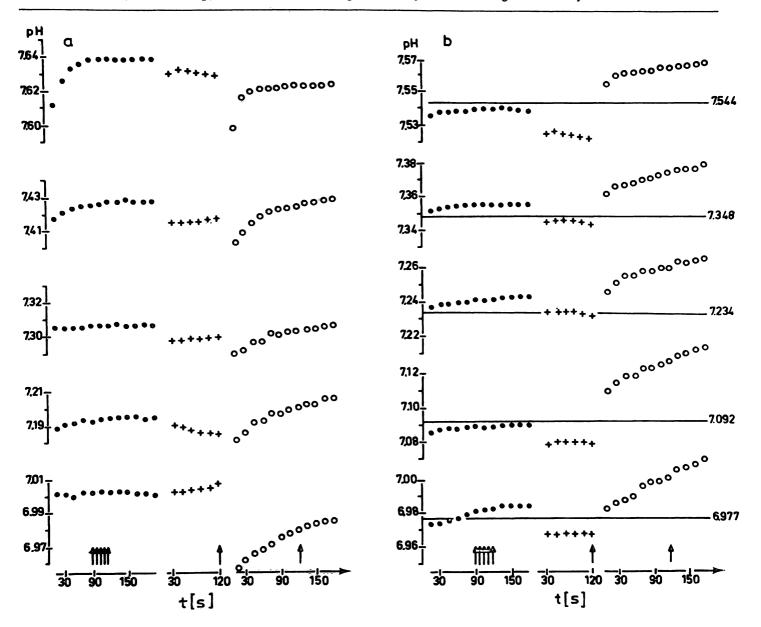


Fig. 1. pH response curves of blood (a) and buffer AIII (b). Each symbol is the mean of a duplicate. Arrows indicate at which time pH values of tonometered samples were read for the rest of this study. The horizontal lines in the graph of buffer AIII indicate calculated pH values (18).

 \bullet = IL-413 + = ABL-1 \circ = AVL-937C

remaining 0.015 pH unit could have been caused by the above mentioned leakage of carbon dioxide. The negative deviation obtained with blood samples agrees with Voigt's (16) results for human control sera (Versatol, Acid-Base; General Diagnostics). Generally it is quite possible that systematically lower pH values are a result of filling the electrode system with sample only once (21). The pH readings from the second and third filling on the BMS2 electrode were in good agreement and were both higher than the pH reading after the first filling especially at higher pH values, as illustrated in figure 4.

Precision

The standard deviations of the pH values of buffer solution at six pH levels (n=5) was less than 0.005 of a pH unit. The same result was found for the standard

deviation of the pH duplicates of 52 blood samples (tab. 2).

pCO_2

Response curves

The response curves of the pCO_2 electrodes for blood and buffer samples are shown in figure 5. The shape of the curves is similar for both media and characteristic for each instrument: decreasing when the pCO_2 is lower and increasing when pCO_2 is higher than the pCO_2 value of the calibration gas. On the IL the best approximation to the calculated values is achieved at "ready" time. This signal coincides with the "data" signal because the pCO_2 electrode has the slowest response in comparison with the pH and the pCO_2 electrodes. The printed pCO_2

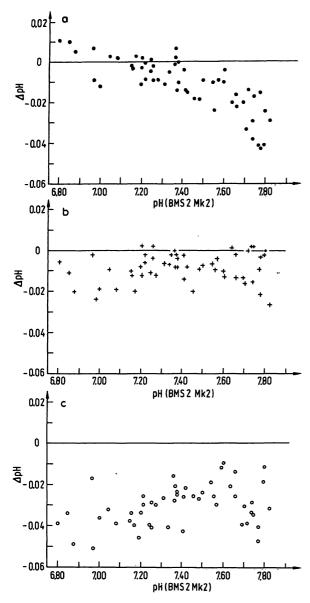


Fig. 2. Results of pH measurements for blood. The pH values measured on IL (a), ABL (b) and AVL (c) minus the pH measured on the BMS 2 are plotted on the y-axis.

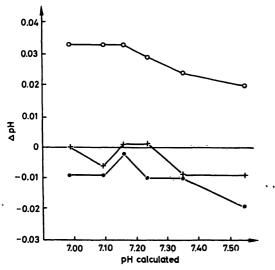


Fig. 3. Results of pH measurements for buffer AIII. The calculated pH is plotted on the x-axis and the difference between measured and calculated pH on the y-axis.

• = IL-413 + = ABL-1 0 = AVL-937C

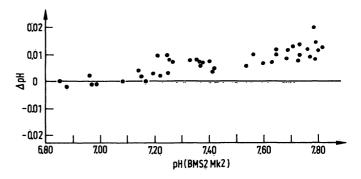


Fig. 4. The mean of the second and third pH reading minus the first pH reading as a function of pH level for blood with the micro glass electrode of BMS 2-Mk 2.

Tab. 2. Precision of pH, pCO₂ and pO₂ measurements

Sample	Instrument	pH	$\frac{\text{pCO}_2}{\text{CV}^2}$	$\frac{pO_2}{CV^3}$
		S.D. ¹)	CV-)	CV°)
			[%]	[%]
	IL	< 0.005	0.7	1.4
Blood	ABL	< 0.005	0.7	1.4
	AVL	< 0.005	1.8	1.7
	IL	< 0.005	0.5	2.8
AÏIÏ	ABL	< 0.005	1.5	2.5
	AVL	< 0.005	1.2	3.0

1) S.D. was calculated from a_{H+} values. 52 duplicate values were used for blood, and mean values at six pH levels for 5 measurements were used for buffer AIII.

2) The mean reproducibility (CV) was established by averaging the coefficient of variation (CV) of six pCO₂ levels from 14-106 mm Hg (blood n = 30, buffer AIII n = 5 at each level).

3) The mean reproducibility (CV) was established by averaging the coefficient of variation (CV) of eight pO₂ levels from 0-642 mm Hg (blood n = 30, buffer AIII n = 5 at each level).

values of the ABL are the best approximation to the calculated values. The readings on the AVL over the whole pCO₂ range were performed at 120 s, because for both high and low pCO₂ values a plateau value was reached within 120 s, in correspondence with the "ready" indication.

We may generally conclude that the optimum reading time of the pCO₂ values agrees with the specifications of the manufacturers.

Accuracy

Table 3 presents the parameters for the linear regression analysis between calculated and measured pCO_2 values for the range up to about 100 mm Hg, which demonstrate a good correlation (r = 0.99) but a positive y-intercept. The accuracy of the pCO_2 measurement on different pCO_2 levels is illustrated in figure 6. The deviation of the measured pCO_2 from the calculated value is influenced by the pCO_2 of the last calibration gas (about

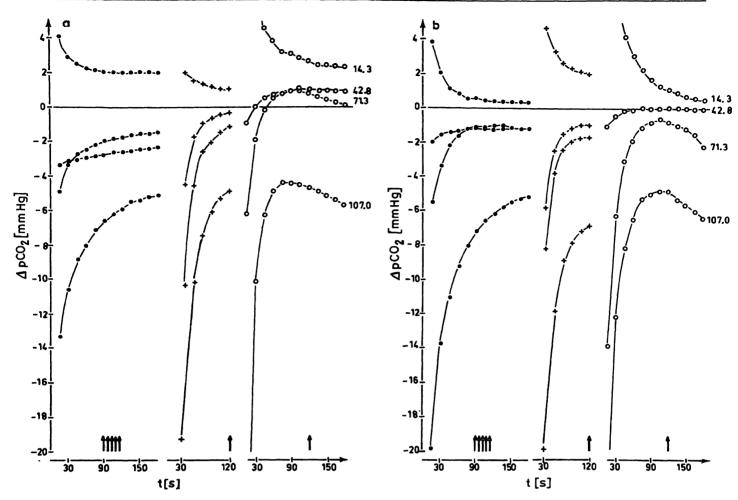


Fig. 5. pCO₂ response curves of blood (a) and buffer AIII (b). The difference between measured and calculated pCO₂ is plotted on the y-axis. Each symbol is the mean of a duplicate. The figures on the right side of the curves indicate the calculated tonometer pCO₂ values. Arrows indicate at which time pCO₂ values of tonometered samples were read.
 = IL-413 + = ABL-1 = AVL-937C

Tab. 3. Parameters of linear regressions of calculated (x) and measured (y) pCO₂ and pO₂

	Sample	Instrument	Slope	y-Intercept	r	n
		IL	0.87	4.08	0.998	18
	Blood	ABL	0.91	1.95	0.999	18
		AVL	0.93	3.18	0.998	18
pCO ₂ 14-106						
mm Hg		IL	0.85	6.18	0.996	6
	AIII	ABL	88.0	4.59	0.996	6
		AVL	0.93	2.06	0.999	6
		IL	0.97	1.23	0.998	18
	Blood	ABL	0.98	2.24	0.998	18
		AVL .	1.04	0.40	0.999	18
pO ₂ 0-130		•			·	
mm Hg		IL	0.71	42.12	0.999	6
	AIII	ABL	0.81	29.28	0.999	6
	-	AVL	0.76	36.66	0.998	6

35 mm Hg) before sampling. This "memory effect", caused by mixing of sample with gas still present in the measuring chamber and the electrode, has already been described by *Berkenbosch* (6) and *Crampton-Smith*

(7, 8). Because this effect is nearly the same for all instruments, a correction can be made for it.

Precision

Table 2 shows the average precision (\overline{CV}) of the pCO₂ at different levels. The coefficient of variation (CV) was better than 2 percent for blood and buffer samples.

pO_2

Response curves

The response curves of the pO₂ electrodes for blood and buffer samples are shown in figure 7. The curves from samples with pO₂ \leq 128 mm Hg reach a plateau after about 30 s, and those with pO₂ \geq 257 mm Hg reach a distinct maximum.

For IL, pO_2 values at time "ready" and "data" are broadly equal at pO_2 levels up to 257 mm Hg. Above this gas tension a better approximation to the calculated pO_2 is obtained if the "ready" value is used.

For ABL, the pO_2 values at print-out time are close to the calculated values. For AVL, the pO_2 value was read at a fixed time of 30 s, because we found that the green light did not indicate adequately.

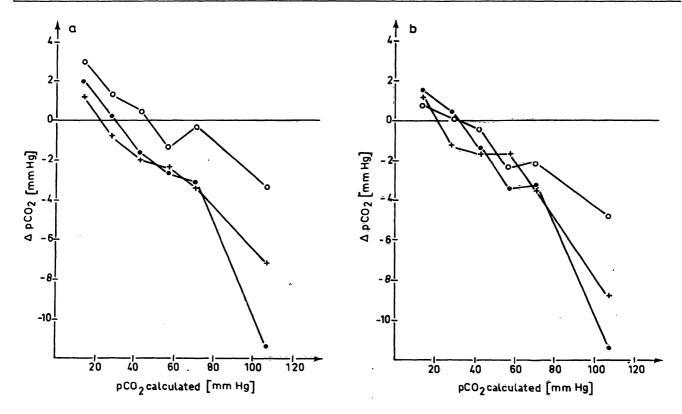


Fig. 6. Results of pCO₂ measurement for blood (a) and buffer AIII (b). The difference between measured and calculated pCO₂ is plotted on the y-axis. For blood each symbol is the mean of 30 measurement, and for buffer AIII it is the mean of 5 measurements

• = IL-413 + = ABL-1 0 = AVL-937C

Accuracy

Table 3 presents the parameters for the linear regression analysis between calculated and measured pO_2 values for the range up to 130 mm Hg. In this range for blood and buffer a linear relationship exists with a correlation coefficient better than 0.99; for buffer solution a large positive y-intercept was found.

Figure 8 illustrates the accuracy of the pO₂ measurements at nine different levels for blood and buffer samples. Up to 130 mm Hg the behaviour of blood and buffer is completely different: for blood, measured values hardly differ from the calculated pO₂ values, whereas for buffer the difference depends on the pO2 level. At levels above 130 mm Hg, both blood and buffer showed an increase of negative difference with increasing pO2 level. This different behaviour can be explained by the presence of the residual calibration gas (about 140 mm Hg) in the measuring chamber. For buffer samples tonometered with lower or higher pO₂ than the pO₂ of the last calibration gas, measurements will be higher or lower, respectively, than the calculated values, due to contamination with the residual gas. For blood this effect is small at low pO₂ values (< 100 mm Hg), as hemoglobin will act as a "buffer" to moderate changes in pO2. At pO2 levels above 100 mm Hg hemoglobin is fully saturated, so pO2 changes will primarily affect physically dissolved, rather than chemically bound oxygen; i.e. blood samples behave like buffer samples. Figure 9

shows the marked influence of the calibration gas on the measured pO_2 of buffer and, to a lesser extent of blood samples for the IL blood gas analyser. Gas-fluid differences, not optimal polarizing conditions for the electrode, and residual gas in the measuring chamber can be held reponsible for the discrepancies between the measured and calculated values. It can be seen that blood samples with a pO_2 in the physiological range can be measured more accurately with a calibration gas of a pO_2 of 140 mm Hg instead of the pO_2 of 70 mm Hg recommended by the manufacturer.

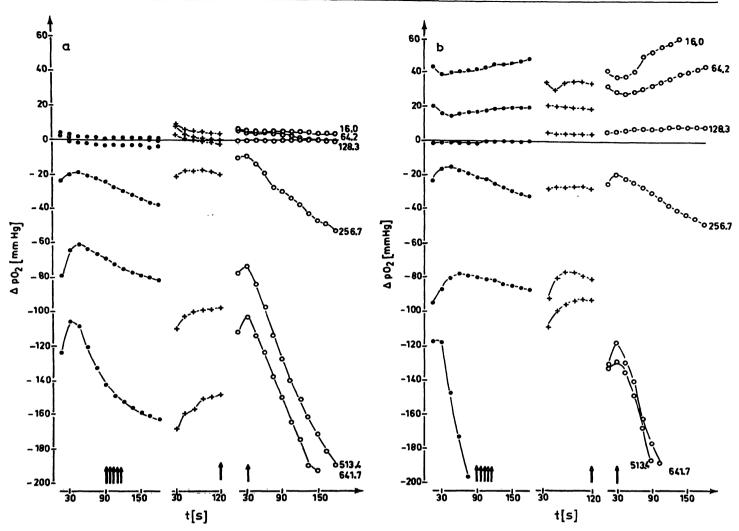
Generally speaking, standardization of the calibration with a fixed pO_2 of about 140 mm Hg might be an improvement. Flushing of the measuring chamber (2–3 times) with sample, which is only possible for IL in the manual mode, is a way oa diminishing the residual gas effect.

Precision

Table 2 shows the average precision (\overline{CV}) of the pO₂, which is better than 2% for blood and 3% for buffer samples.

Operating notes

During the evaluation period, the instrumentation was well maintained by checking all electrode systems and renewing membranes each two weeks.



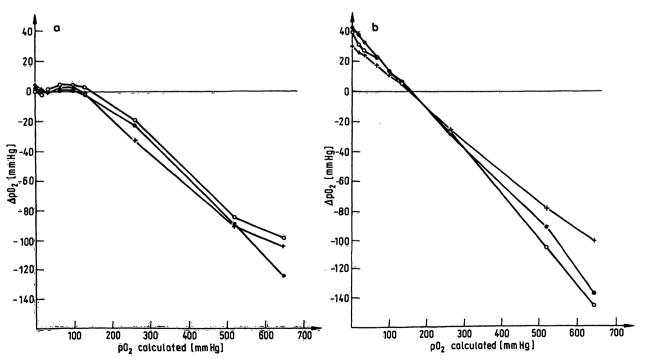


Fig. 8. Results of pO₂ measurement for blood (a) and buffer AIII (b). The difference between measured and calculated pO₂ is plotted on the y-axis. For blood each symbol is the mean of 30 measurements, and for buffer AIII it is the mean of 5 measurements.

• = IL-413 + = ABL-1 ∘ = AVL-937C

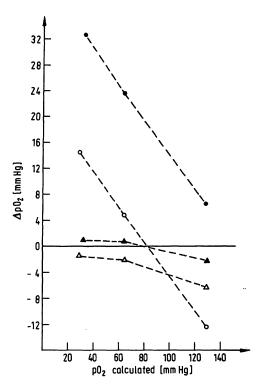


Fig. 9. The influence of the calibration gas on the results of pO₂ measurement with IL for blood and buffer AIII. The difference between measured and calculated pO₂ is plotted on the y-axis. Triangles (A, A) correspond to blood and dots (A, O) to buffer AIII. Open symbols indicate results obtained after calibration of the electrode with 10% O₂ and closed symbols results obtained after calibration with 20% O₂.

Comments on individual instruments *IL-413*

We had the opportunity to obtain experience with two IL instruments and a third one in routine use and found that the IL is easy to operate. A good filling of the system with sample can easily be controlled by visual inspection because the sample pathway and electrodes are mounted in a transparant thermostated waterbath. Most parts of the measuring circuit are readily accessible, which is an advantage especially for cleaning the easily clogged valves.

A serious problem might be gas bubbles left in the pCO_2-pO_2 measuring chamber after sampling proteinfree tonometered buffer solutions, thus causing erroneous results. We solved this problem in one instrument by boring the top of the chamber to a cone shape.

From standby position a complete calibration or a simple calibration (cal 1) with a sample measurement in duplicate can be performed in about 4 min. Although according to the manual, a $100 \mu l$ sample is sufficient in the "micro" mode, we found that about three capillary samples (total $250 \mu l$) are needed to obtain reliable pH and blood gas results. It might be possible to improve operation by calibrating the glass electrode for electrical zero with buffer "7.384" and establishing the slope with buffer "6.840".

ABL-1

This instrument is simple to operate, in consequence of its automation and computerisation, and it has proved trustworthy during one year of observation. The operator can hardly influence the results. The inside of the electrode chamber cannot be inspected visually and is accessible with difficulty, which is inconvenient when changing the membranes of the gas electrodes.

A complete calibration is done automatically every two hours. This does not imply that false calibrations are excluded. Dust in the gas mixing apparatus may alter the composition of the calibration gases, which results in different pCO₂ and pH values for the equilibrated buffer solutions. The calculator does not correct for this and apparent values are printed out. Once we found a difference of 0.06 of a pH unit which could be easily detected using daily tonometered buffer solution for quality control (18, 19). In this case the gas mixing apparatus had to be replaced. The electrical checking of the electrodes through switching off the main power, which leads to temperature drop, and cleaning the computer memory, might be better performed with a separate switch instead of the main power switch.

AVL-937C

We have had two apparatus at our disposal. As already mentioned the adjustment of indication lights of both instruments was not sufficient Also the instability of the readings on the digital screen caused by static electricity was inconvenient. Simultaneous calibration of pH and gas electrodes is not possible which is a disadvantage in comparison with IL and ABL. With our modifications for calibration and measurement the time needed to perform a complete calibration is about 30 min. Once this calibration had been done, the electrodes were found to be very stable with respect to calibration buffers and gases during the day. So between measurements a single calibration for pH pCO₂ and pO₂ is sufficient and takes about 10 min, when done in duplicate.

In "standby" position gas 1 is flowing through the capillary measuring chamber in which the electrode tips are located. Although this results in a very stable signal for the pCO₂ electrode (7) and pO₂ electrode, it will interfere with pH measurement. The time needed to stabilize the pH electrode after a gas flow during the night is about 15 min. We found the same phenomenon for the gas electrodes if buffer is left in the measuring chamber overnight. The fact that the measuring chamber is rinsed with distilled water between measurements will easily give rise to a contaminating film of protein and might be better performed with saline.

An advantage of the AVL is its suitability for micro samples.

Concluding remarks

The evaluated new generation of pH-blood gas analysers: IL-413, ABL-1 and AVL-937C represent a great advance, in that pH, pCO₂ and pO₂ may be measured simultaneously and automatically in one sample of blood. The analytical variables: response time, accuracy and precision of their electrode systems are comparable, with the exception of the pH response and pH difference of AVL. The IL is the fastest apparatus, the ABL is easiest in operation and the AVL most adapted to micro samples. In the (patho)physiological range all instruments may provide suitable results to the clinician.

However, when more accurate values are needed in acid base balance and oxygen transport evaluation, we feel that this instrumentation has to be standardized and improved. To achieve this we suggest the following electrode alterations:

- pH The electrode glass should have a standard composition to avoid systematic errors. The importance of using a saturated KCl bridge, free of contamination should be emphasized, because a lower salt concentration lowers the results (11).
- pCO₂ To minimize gas exchange with the electrode electrolyte and consequently the "memory" effect, the space between the glass electrode and the holder should be very small (22). It seems also justified to apply correction factors since the deviations of different electrodes are the same as shown in this study.

pO₂ Unfortunately the response of this electrode is not linear with the oxygen concentration in fluids. It seems that the optimal conditions of polarography, well studied in the beginning of the history of macro electrodes (23), are not generally known for micro electrodes. Recently *Hahn* et al (24) showed in a careful study, examining the electrode reaction in some detail, that non-linearity of micro pO₂ electrodes is due to the absence of a plateau on the polarogram, when used with conventional electrolytes.

The use of electrolyte of pH 11.2 and a voltage of about -1.0 V results in a long, flat plateau and a marked improvement in both electrode linearity and response time; the use of this procedure is advisable.

Further, calibration of the electrodes should be uniform. Buffer solutions equilibrated with gas mixtures, as used in the ABL, seem most suitable. Last but not least, a good quality control program should be developed to interpret optimally the pH and blood gas values, obtained.

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