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Electrodes for 24 hour pH monitoring – a comparative study

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SUMMARY Three pH electrodes in clinical use were examined – (1) antimony electrode with remote reference electrode (Synectics 0011), (2) glass electrode with remote reference electrode (Microelectrodes Inc. MI 506) and (3) combined glass electrode with integral reference electrode (Radiometer GK2801C). *In vitro* studies showed that both glass electrodes were similar and superior to the antimony electrode with respect to response time, drift, and sensitivity. The effect of the siting of the reference electrode on the recorded pH was examined in five human volunteers. The pH reading using a remote skin reference electrode was higher by a mean of 0·3 pH units (range 0·0–0·6) in the stomach, lower by 0·65 pH units (0·5–0·8) in the duodenum and lower by 0·3 pH units (0·0–0·6) in the oesophagus than that simultaneously obtained with an intraluminal reference electrode. Buccal reference electrodes gave similar readings to skin. Combined reference and glass pH electrodes are recommended for 24-hour ambulatory pH monitoring.

Ambulatory pH monitoring of the upper gastrointestinal tract is being used increasingly both for diagnostic purposes and as a research tool. The procedure involves the use of an intraluminal sensing electrode and a reference electrode which are connected to a recording device. Various types of electrodes are commercially available for gastrointestinal work but glass and antimony electrodes are the most commonly used. pH monitoring systems also differ in the siting of the reference electrode. The antimony electrode and some glass electrodes utilise a remote reference attached to the skin of the chest wall whereas with the combined glass electrode the reference is intraluminal, adjacent to the sensing electrode. A recent international workshop has highlighted the lack of independent information concerning the relative merits of these different recording systems.[1]

We have examined *in vitro* the performance of the three most commonly used electrodes and have assessed the effect on the recorded pH of the siting of the reference electrode.

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Methods

MATERIALS

The following three electrodes were examined (Fig. 1): (1) Antimony electrodes (Synectics Medical, No. 0011) employing a remote reference electrode, (2) Glass electrodes (Microelectrodes Inc. MI 506) employing a remote reference electrode, (3) Glass electrodes (Radiometer, GK 2801C) with combined sensing and reference electrodes.

IN VITRO STUDIES

The basic operating characteristics – that is, response time, sensitivity, and drift of the three different types of electrodes were assessed. For electrodes other

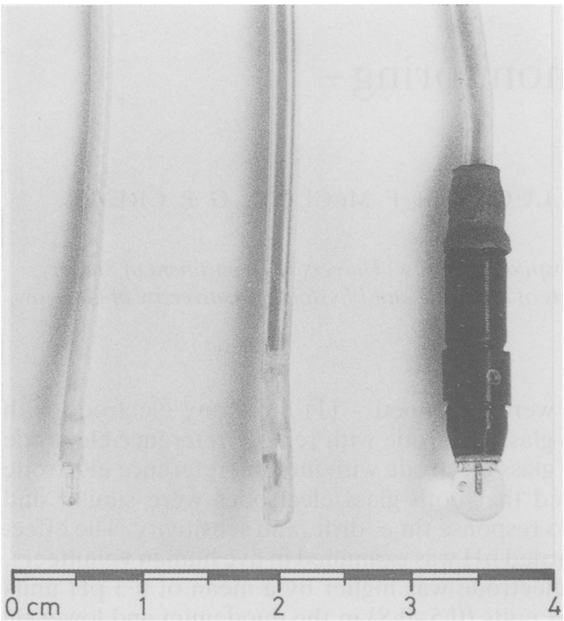

Fig. 1 *Microelectrodes Inc. glass electrode is shown on the left, the Synectics antimony electrode in the centre, and the Radiometer combined glass electrode on the right. Each division on the scale represents 1 cm.*

than Radiometer glass electrodes, a calomel electrode with an agar bridge was used as the reference electrode.

Response time

Response time was measured by transferring the electrodes between stirred buffers of pH 7 (Synectics No. 5001) and pH 1 (Synectics No. 5002) at 37°C. The electrodes were connected to an electrometer (Keithley 610C) and the results plotted using a paper chart recorder (Speedomax XL682). As the presence of artifact at the time of transfer of the electrodes may obscure the tracing, the response time was defined as the time taken for the electrode voltage to go from 10% to 90% of its final value. Six models of each type of electrode were examined and measurements made in triplicate on each individual electrode to obtain an average value per electrode. Values for a group of similar electrodes are presented as the mean and standard error of these average values. The study was repeated in unstirred buffers at 22°C.

The effect on response time of gastric juice, duodenal juice, and a combined antacid/local anaesthetic preparation (Mucaine: Wyeth Laboratories) was investigated by transferring the electrodes from each of these test solutions to a stirred buffer of known pH at 37°C.

Sensitivity

Sensitivity – that is, mV response per pH unit, was assessed in six electrodes of each type over the pH range 1 to 7. The antimony electrode is irreversibly damaged by many of the standard buffers normally used in calibration, for example phosphate or phthalate.[2] Buffers compatible with the antimony electrode are only available for pH 1 and pH 7. For this reason a titration method was used for each electrode to measure sensitivity between these pH values. The recorded potential differences (mV) of the various electrodes were plotted against pH recorded with a standard glass electrode (Pye-Unicam 401) during titration from pH 7 to pH 1 and back at 37°C.

The sensitivity of the two types of glass electrode in mV/pH was calculated from the slope of the resultant graph. This was not possible for the antimony electrode because of the non-linear characteristics obtained and therefore the sensitivity was calculated by dividing the difference in readings (mV) at pH 1 and 7 by 6.

Drift

After calibration in buffers at pH 7 and pH 1, a single continuous 24 hour recording was made from each electrode during immersion in a stirred buffer at 37°C. Once again, six examples of each type were studied. Drift was defined as the maximum excursion in pH readings over the 24 hours.

HUMAN STUDIES

The extent to which the siting of the reference electrode leads to differences in recorded pH was examined in five fasted healthy human volunteers. This involved the use of a combined glass electrode (Radiometer, GK 2801C), a Ag/AgCl skin reference electrode and gel (Hellige GMBH, D7800 Freiburg iB, W Germany) and two digital recorders (Digitrapper MKII, Synectics Medical). The pH sensing electrode of the combined glass electrode was connected to both recorders. The intraluminal reference electrode of the combined glass electrode was connected to one recorder and the skin reference electrode to the other. This permitted simultaneous recording from the same pH electrode using different reference sites.

The electrode was passed into the duodenum under radiographic screening and recordings made from duodenum, stomach and oesophagus. The study was then repeated using a Ag/AgCl buccal reference electrode (Pye-Unicam 340) in place of the skin reference electrode. The statistical significance of differences in the mean values was assessed using the non-parametric Mann-Whitney U test.

Results

IN VITRO STUDIES

Response Time

Each of the electrodes had a rapid response time of less than 0·5 second on transfer from pH 7 to pH 1 (Table 1). The response times of the Microelectrodes Inc. and Radiometer glass electrodes, on transfer from pH 1 to pH 7 were similar, being 0·5±0·1 second (mean±SEM) and 0·8±0·1 second respectively. The response of 3·4±0·8 seconds for the antimony electrode over the same pH range, however, was significantly slower ($p<0·025$) than either of the glass electrodes.

When the pH 1 to pH 7 response times were repeated using unstirred buffers at 22°C, in place of the stirred buffers at 37°C, they were all prolonged, at 3·25±1·0 seconds, 20±8 seconds and 160±24 seconds for Microelectrodes Inc., Radiometer and antimony electrodes respectively (Table 1).

For each electrode the response time on moving from duodenal juice (pH 6·5) to buffer pH 1 was similar to transfer from buffer pH 7 to buffer pH 1 (Table 1). Likewise, the response time on moving from gastric juice (pH 1·5) to buffer pH 7 was similar to transfer from buffer pH 1 to buffer pH 7. Each electrode showed a slower response on moving from Mucaine (pH 7·6) to buffer pH 1, however, than on transfer from buffer pH 7 to buffer pH 1. In comparison with their response times of <0·5 second on transfer from buffer pH 7 to buffer pH 1, the response time of each electrode was prolonged on transfer from Mucaine to buffer pH 1 with values ranging from 1–54 seconds. The Mucaine affected the three types of electrodes to a similar degree, though there were marked differences between individual electrodes, and even between the same electrode studied on different occasions.

Sensitivity

The Microelectrodes Inc. and Radiometer glass electrodes were similar with respect to sensitivity, with values of 54·9±1·7 and 55·1±1·7 mV/pH unit respectively. The antimony electrode was less sensitive than either glass electrode ($p<0·02$) with a value of 47·6±1·0 mV/pH unit (Table 2). Both glass electrodes showed a linear response over the pH range 1 to 7, but that of antimony was non-linear and showed a consistent hysteresis (Fig. 2).

Drift

The drift of both glass electrodes was similar (0·11±0·01 (range 0·0–0·25) and 0·13±0·05 (range 0·0–0·2) pH units/24 hours for Microelectrodes Inc. and Radiometer respectively) and less than that of antimony (0·47±0·13 (range 0·1–0·6) pH units/24 hours) ($p<0·05$).

HUMAN STUDIES

Using the Radiometer electrode with its combined reference electrode, the median duodenal pH recorded was 6·4 (range 5–7·5), the median gastric pH 1·5 (range 1–2) and the median oesophageal pH 6·8 (range 6–7·5). The simultaneous pH readings obtained with the skin reference electrode were different, being lower by a mean of 0·65 pH units (range 0·5–0·8) in the duodenum, higher by a mean of 0·3 pH units (range 0–0·6) in the stomach and lower by a mean of 0·3 pH units (range 0–0·6) in the oesophagus.

When a buccal reference was used, the duodenal recordings were lower by a mean of 0·7 pH units (range 0·2–1), those from the stomach higher by a mean of 0·2 pH units (range 0–0·4) and those from the oesophagus lower by a mean of 0·3 pH units (range 0–0·6) compared with the recordings obtained from the combined electrode.

Discussion

Glass electrodes have been used for monitoring gastrointestinal pH for more than 40 years[3,4] and over this time have been modified considerably to improve their performance and reduce their size. During the past 10 years, there has been increased interest in the monocrystalline antimony electrode[5] and it is now

Table 1 *Response times of the three types of electrodes under different conditions*

		10–90% response time (sec)		
From	*To*	*Glass (Microelectrodes Inc.)*	*Glass (Radiometer)*	*Antimony (Synectics)*
Buffer pH 7	Buffer pH 1	<0·5	<0·5	<0·5
Buffer pH 1	Buffer pH 7	0·5±0·1	0·8±0·1	3·4±0·8
Buffer pH 1 (unstirred 22°C)	Buffer pH 7 (unstirred 22°C)	3·25±1	20·8±8	160±24
Duodenal juice pH 6·5	Buffer pH 1	<0·5	<0·5	<0·5
Gastric juice pH 1·5	Buffer pH 7	1·0±0·2	0·8±0·1	4·5±0·7

Values are mean±SEM; for significance values see text; all experiments were performed in stirred solutions at 37°C except where indicated to contrary in parenthesis.

Table 2 *Comparison of the sensitivity and drift of the three types of electrodes*

Electrode type	*Sensitivity (mV/pH unit)*	*Drift (pH units/24h)*
Antimony	47·6±1·0	0·47±0·13
Glass (Microelectrodes)	54·9±1·7†	0·11±0·01*
Glass (Radiometer)	55·1±1·7†	0·13±0·05*

Values are mean±SEM. *Significantly different from antimony value at p<0·05; †significantly different from antimony value at p<0·02.

used widely by gastroenterologists. In spite of the lack of properly controlled comparative studies, it has been claimed that antimony electrodes are comparable with or even superior to the more conventional glass electrodes both in their basic electrode characteristics and also in the ease with which they can be used in a clinical practice.[6] Our study shows that the performance of the antimony electrode is inferior to that of glass electrodes with respect to response time, sensitivity and drift.

Although each of the three types of electrodes showed a rapid response on moving to a more acid pH, the antimony electrode was significantly slower than the glass electrodes on moving to a more alkaline pH. These response times were obtained under the optimal conditions of a stirred solution at 37°C. In unstirred solutions at 22°C, the response time of the Microelectrodes Inc. electrode was only slightly prolonged by approximately three seconds, that of the Radiometer by 20 seconds, whereas that of antimony was markedly prolonged by 160 seconds. The difference in response times between the glass electrodes in unstirred solutions is most probably explained by the greater volume of buffer carried by the larger electrode during transfer. The argument does not hold for the small antimony electrode, the longer response time of which may reflect local unstirred layer effects at the sensing surface. The shape of the electrode may alter the adherent volume close to this surface. Another factor may be the local accummulation of the products of the oxidation-reduction reaction known to take place at the surface of this electrode. Whatever the reason, it is noteworthy that these electrodes would have shown a slower response time in conditions likely to occur during *in vivo* measurement. In addition, the temperature dependence of antimony is such that a difference of 0·55 pH unit exists between readings at 37°C and 22°C, compared with a difference of only 0·05 pH unit for glass.[7] In an area of the gastrointestinal tract like the stomach, in which there is incomplete mixing of contents and marked variations in temperature, the discrepancy between glass and antimony electrodes may be even greater.

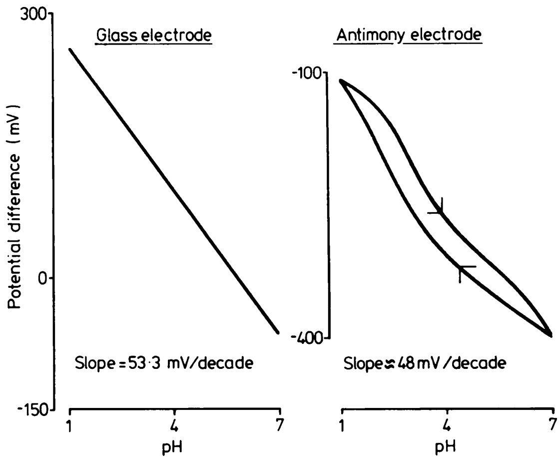

Fig 2. *Sensitivity of a representative glass electrode and a representative antimony electrode.*

The observation that the response times of the three electrodes were unaffected by gastric or duodenal juices, is in agreement with previous studies.[8] The prolongation of the response time by Mucaine is of particular relevance to ambulatory oesophageal pH studies as use of this medication could complicate their interpretation. The effect of other mucosal coating agents requires to be studied.

The commercially available systems using antimony electrodes assume linearity between pH 1 and 7, but this was found not to be the case. The resultant error is compounded by the hysteresis effect. This means that if the electrode moves to a solution of – for example, pH 4 from a solution of pH 7 a different reading will be obtained than if the electrode had been transferred from a solution of pH 1. These differences in the pH range 3 to 6 were often in the order of 20 mV, which would represent a difference of 0·4 pH units. Such an error in recorded pH would significantly affect the assessment of oesophageal reflux which is usually defined as duration and frequency below pH 4. Glass electrodes, in contrast, showed a linear response and hysteresis was absent.

The more marked drift of the antimony electrode may be due to oxidation of the antimony surface over the 24 h recording period.[9] As a result of this visible surface damage, the antimony electrode requires careful cleaning to maintain its performance. Glass electrodes are unaffected by such chemical reactions.

Our human studies highlight the large differences in recorded pH which may occur when skin reference electrodes are used as opposed to intraluminal reference electrodes. This effect has been previously noted and attributed largely to transmucosal potential differences which vary between oesophagus, stomach and duodenum.[10–12] Buccal reference electrodes have been used in preference to skin electrodes in an attempt to overcome this problem,[13] but our study shows that they have no advantage.

Although the difference in recorded pH with skin and intraluminal reference electrodes may be partly explained by the transmucosal potential difference, the different junctional potentials at the skin reference electrode and intraluminal reference electrode may also contribute to the discrepancy.[14]

In summary, we have found that the performance of glass electrodes is superior to that of antimony electrodes. The inferior operating characteristics of antimony will contribute a larger error to clinical recordings, particularly when there are rapid changes in pH or when recordings are analysed as time above or below a specific pH value. In addition, significant differences in recorded pH occur when skin or buccal reference electrodes are used in place of intraluminal electrodes. In order to improve accuracy we recommend the use of glass electrodes and to allow comparison of results from different centres, we recommend combined glass electrodes for prolonged monitoring.

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