An evaluation of the electrochemical oxygen probes used in steelmaking

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SYNOPSIS

Some of the important properties of solid electrolytes that influence the performance of electrochemical oxygen probes are discussed in the first part of this paper. It is shown that accurate and reproducible measurements of oxygen in liquid steel are possible with commercial oxygen probes only if great care is exercised in the make-up of the chemical and phase composition, as well as the microstructure of the solid electrolytes used in these probes.

To prove this premise, the second part of this study reports on the results of an experimental evaluation of a new commercially available oxygen probe. An evaluation of the solid electrolytes used in this probe indicated that the consistency of the chemical composition, degree of stabilization, and microstructure of the electrolytes used are well controlled. The successful application of this particular oxygen probe under industrial conditions was confirmed. It was also found possible to make reliable and reproducible measurements, with acceptable uncertainty, by proper handling of the probe.

Some recommendations are made as to the interpretation of the e.m.f. response curve and the use of the electronic processing unit supplied with the probe.

SAMEVATTING

In die eerste deel van hierdie artikel word sekere van die belangrike eienskappe van vastestofelektroliete wat die suksesvolle werking van elektrochemiese suurstofsensors beïnvloed, bespreek. Daar word getoon dat akkurate en herhaalbare suurstofbepalings met kommersiële suurstofsensors slegs moontlik is indien die chemiese samestelling, faseverhouding, en mikrostruktuur van die vastestofelektroliet wat in die suurstofsensor gebruik word, altyd konstant gehou word.

Ten einde hierdie gevolgtrekking te bevestig, word in die tweede gedeelte van hierdie artikel die resultate van 'n eksperimentele evaluering van 'n nuwe kommersiële suurstofsensor bespreek. 'n Evaluering van die vastestofelektroliete wat in hierdie besondere sensor gebruik word, het getoon dat die chemiese samestelling, mate van stabilisering, en mikrostruktuur van verskillende elektroliete konstant bly. Die suksesvolle gebruik van die betrokke suurstofsensor onder nywerheidstoestande is bevestig. Dit was moontlik om betroubare en herhaalbare metings met 'n aanvaarbare onsekerheid te verkry deur die sensor korrek te hanteer.

Enkele aanbevelings word gemaak ten opsigte van die interpretasie van die e.m.f. respons-kurwe en die gebruik van die elektroniese verwerkingseenheid wat saam met die sensor verskaf word.

Introduction

If one parameter has to be singled out as the most important in the control of steelmaking processes, it would probably be oxygen. The various metallurgical stages of steelmaking can essentially be regarded as reduction and oxidation processes. Since the level of dissolved oxygen characterizes the degree of oxidation of the liquid steel, a proper knowledge of this quantity in the various stages of steelmaking is imperative.

Conventionally, oxygen in liquid steel is determined on solid samples taken from the liquid steel, by neutron-activation analysis or by chromatographic analysis of the oxygen liberated during fusion of the sample[1]. The disadvantage of these methods is that the oxygen content so determined includes the dissolved oxygen as well as the oxygen present in the form of oxide inclusions. Consequently, the actual degree of oxidation of the steel bath cannot be determined explicitly. This method of analysis is also time-consuming since approximately 10 minutes elapse before the results of the analysis are available to the steelmaker. However, it has recently become standard practice in modern steelplants to use electrochemical oxygen probes for the determination of dissolved oxygen. Since the activity of the dissolved oxygen is measured directly by this electrochemical technique, the degree of oxidation of the steel bath can be determined quantitatively. A measurement is made within 10 seconds, and steelmakers are therefore provided with a means of direct control over oxidation in the liquid steel.

Electrochemical oxygen probes for the in situ determination of dissolved oxygen in liquid steel are used successfully in various parts of the world[2-5]. In Japan, for example, more than 300 000 commercial oxygen probes are employed annually[6]. In South Africa, on the other hand, commercial oxygen probes are used only on a very limited scale. This may be due, in part, to various problems encountered in the industrial application of commercial oxygen probes. Several local steelmakers have reported problems associated with the accuracy and reproducibility of measured oxygen levels[7]. For example, it has been reported that oxygen levels measured simultaneously with two identical oxygen probes in the same ladle indicated significantly different oxygen activities. However, an improved oxygen probe was introduced recently that, according to the manufacturer, has overcome the problems associated with earlier designs.

These factors provided the stimulus for a joint in-

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vestigation by industry and the Pyrometallurgy Research Group at the University of Pretoria into the reliability and possible applications of commercial oxygen probes under local steelmaking conditions[7].

The successful application of electrochemical oxygen probes depends to a large extent on a thorough understanding of the fundamental principles of their operation and an appreciation of their limitations. Accordingly, the first part of this paper is devoted to a consideration of some of the important factors influencing the performance of electrochemical oxygen probes. In the second part, the results of an experimental evaluation of a new commercial oxygen probe are reported.

The Performance of Electrochemical Oxygen Probes

The electrochemical oxygen probe generally used to determine the oxygen activity of liquid steel can be expressed as

$$Cr + Cr_2O_3/ZrO_2-MgO/(O)_{liquid\ steel}, \dots\dots\dots (cell\ I)$$
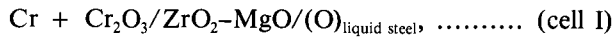
where

ZrO_2-MgO is a magnesia-stabilized zirconia solid electrolyte,

Cr + Cr_2O_3 is a reference electrode of known oxygen potential, and

$(O)_{liquid\ steel}$ is a liquid-steel electrode of unknown oxygen potential.

For the ideal case where the solid electrolyte exhibits pure ionic conduction and thermodynamic equilibrium exists at the electrolyte–electrode interfaces, the e.m.f. of cell I is given by the well-known Nernst equation

$$E = \frac{RT}{4F} \ln \frac{P''O_2}{P'O_2}, \dots\dots\dots\dots\dots\dots\dots (1)$$

where $P''O_2$ and $P'O_2$ are the equilibrium partial pressures of oxygen in the liquid steel and reference electrode respectively, R is the gas constant, F the Faraday constant, and T the absolute temperature. It is evident from equation (1) that the oxygen potential of a steel bath can be determined by experimental measurement of the temperature and e.m.f. of the oxygen probe. However, there are some important factors that may impede the successful application of electrochemical oxygen probes.

Since oxygen probes are at ambient temperature when immersed in a steel bath, the e.m.f. signal changes with time until equilibrium conditions are attained in the reference electrode, as well as in the solid electrolyte. Fig. 1 is an example of a typical e.m.f. response curve from an oxygen probe used for the measurement of oxygen in liquid steel. In practice, the accurate measurement of oxygen activity can be ensured only if the e.m.f. response has a stable e.m.f. plateau, a short response time, and good reproducibility. Accordingly, the e.m.f. response curve is one of the important criteria by which the performance of electrochemical oxygen probes should be evaluated. Since the e.m.f. response of an electrochemical oxygen probe is strongly influenced by the inherent properties of the solid electrolyte, and since the solid electrolyte plays such a key role in the performance of an oxygen probe, it is important to analyse some of the relevant properties of solid electrolytes in more detail. Particular attention will be given to the properties that
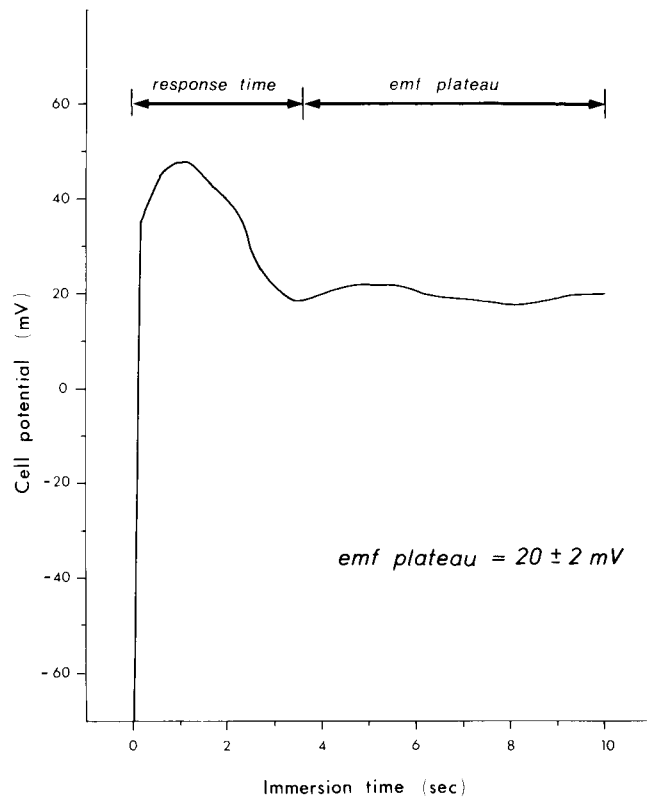

Fig. 1—Typical e.m.f. response of an electrochemical oxygen probe

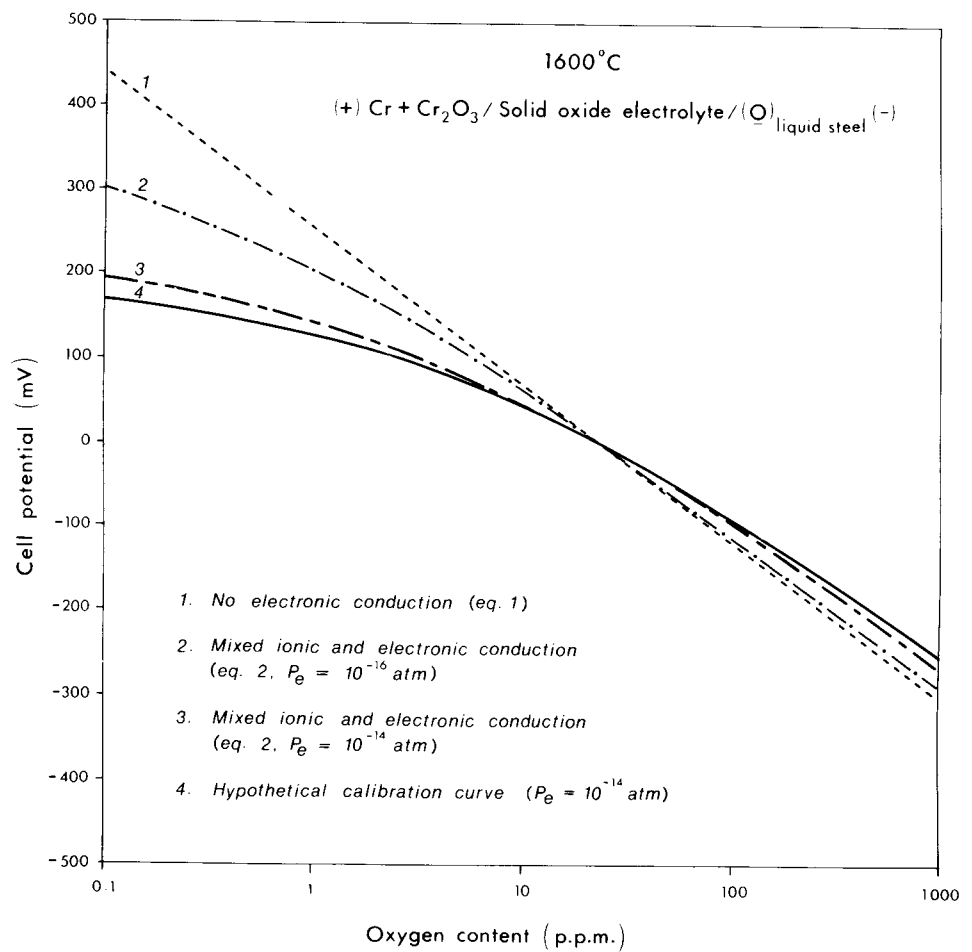are of importance in steelmaking operations.

Electronic Conduction in the Solid Electrolyte

Many of the problems encountered with the stability and reproducibility of the e.m.f. response can be attributed to electronic conduction in the solid electrolyte. In the range of low oxygen potentials existing in liquid steel, zirconia-based solid electrolytes are characterized by mixed ionic and n-type electronic conduction[8-11]. Under these conditions, the oxygen probe generates an e.m.f. signal that is influenced by the electrical properties of the solid electrolyte. Schmalzried[12] has analysed the contribution of electronic conduction in the solid electrolyte to the measured e.m.f. of an electrochemical oxygen probe, and has proposed that the e.m.f. in the presence of n-type electronic conduction in the solid electrolyte can be expressed as

$$E = \frac{RT}{F} \ln \left(\frac{(P''O_2)^{1/4} + (P_e)^{1/4}}{(P'O_2)^{1/4} + (P_e)^{1/4}} \right). \dots\dots\dots (2)$$

The parameter P_e is defined as the partial pressure of oxygen at which the ionic conductivity in the electrolyte is equal to the n-type electronic conductivity. The measured e.m.f. signal of the oxygen probe can still be used in the calculation of the oxygen potential of the liquid steel from equation (2), but only if the correct P_e value of the solid electrolyte is known. In order to illustrate the influence of variations in the P_e value on the e.m.f. signal, and consequently on the calculated oxygen content of the steel, theoretical cell potentials were calculated for cell I as a function of the dissolved oxygen content in the liquid steel for different P_e values[7]. The

Fig. 2—Calculated cell potentials of the cell Cr + Cr₂O₃/solid oxide electrolyte/(O)_liquid steel at 1600°C for different P_e values, and a hypothetical calibration curve for an oxygen probe[7]

1600°C

$(+)$ Cr + Cr$_2$O$_3$/ Solid oxide electrolyte/$(O)_{liquid\ steel}$ $(-)$

Cell potential (mV)

Oxygen content (p.p.m.)

1. No electronic conduction (eq. 1)

2. Mixed ionic and electronic conduction (eq. 2, P_e = 10^{-16} atm)

3. Mixed ionic and electronic conduction (eq. 2, P_e = 10^{-14} atm)

4. Hypothetical calibration curve (P_e = 10^{-14} atm)

results of these calculations are portrayed in Fig. 2. At low oxygen concentrations, the e.m.f. signal of the oxygen probe is significantly influenced by the P_e value of the solid electrolyte. It is therefore imperative, if reproducible and accurate oxygen measurements are to be made, that the P_e value of the solid electrolytes used in electrochemical oxygen probes should be consistent and be known to a high degree of accuracy. (The significance of the calibration curve shown in Fig. 2 is discussed in the following section.)

A further problem that is encountered when a significant amount of electronic conduction is experienced in the electrolyte is that the electrolyte–electrode interfaces may become polarized. If an electrochemical oxygen probe is short-circuited as a result of electronic conduction, oxygen ions are transported through the electrolyte in an attempt to equalize the oxygen potential at the two electrolyte–electrode interfaces. This oxygen has to be supplied to the electrolyte interfaces or removed from them by diffusion but, if the diffusion rate is too slow, equilibrium cannot be maintained and a build-up or depletion of oxygen will occur at the interfaces, as illustrated schematically in Fig. 3. This polarization of the electrolyte–electrode interfaces results in the e.m.f. signal of the probe being lower than the e.m.f. that would be established by the difference in oxygen potentials in the bulk of the electrodes. Since there is strong experimental evidence that polarization of (Cr + Cr₂O₃) reference electrodes as well as liquid steel may occur if a large amount of oxygen is transported through the

electrolyte[8,10,13-16], the electrolyte–electrode interfaces in oxygen probes are most likely to be polarized when

(i) measurements are made in the presence of electronic conduction in the electrolyte, and

(ii) there is a large gradient of oxygen potential across the electrolyte.

Clearly, the use of equation (2) in the calculation of the oxygen content in a bath of liquid steel is not justified in the presence of polarization. However, the inaccuracies resulting from polarization can be overcome by the calibration of oxygen probes according to the e.m.f. measurements obtained under typical plant conditions. An example of such a hypothetical calibration curve, where measured cell potentials are plotted against the analysed oxygen content of the steel melt, is included in Fig. 2 (curve 4).
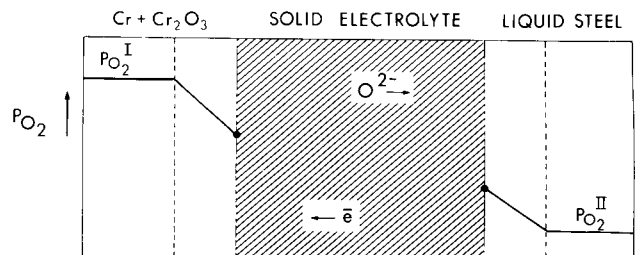

Cr + Cr₂O₃   SOLID ELECTROLYTE   LIQUID STEEL

$P_{O_2}^{I}$

P_{O_2}

O^{2-} →

← e̅

$P_{O_2}^{II}$

Fig. 3—A schematic representation of polarization at the electrolyte–electrode interfaces in an oxygen probe where a (Cr + Cr₂O₃) mixture is used as the reference electrode

The deviation of the experimentally determined values from the theoretical cell potentials, when large cell potentials obtain, can be attributed to polarization of the reference and/or liquid-steel electrodes.

It is important to note that the extent of polarization at the electrolyte–electrode interfaces, and therefore the calibration curve, depends on the flux of oxygen through the electrolyte. The flux of oxygen ions, on the other hand, is a function of the ionic conductivity, the parameter P_e, the dimensions of the solid electrolyte, and the gradient of the oxygen potential in that electrolyte[10,16]. Consequently, a calibration curve is valid only for a given set of electrical properties of the solid electrolyte, again indicating that inconsistent electrical properties of solid electrolytes in electrochemical oxygen probes will result in poor reproducibility and inaccurate oxygen determinations. In the light of the overriding importance of a proper knowledge of the electrical properties of the solid electrolyte used in an oxygen probe, it is important to evaluate some of the factors influencing those electrical properties.

Physical Properties of the Solid Electrolyte

The electrical characteristics of magnesia-stabilized zirconia, the solid electrolyte generally used in oxygen probes, are influenced primarily by the chemical composition of the electrolyte, the impurities in it, and the degree of stabilization and microstructure of the electrolyte. At temperatures above 1400°C, the microstructure of magnesia-stabilized zirconia consists of pure cubic zirconia or a mixture of tetragonal and cubic zirconia, depending on the magnesia content, as shown in Fig. 4. Cubic and/or tetragonal zirconia can also be retained in a metastable condition on cooling, so that the microstructure of the solid electrolytes used in oxygen probes may consist of pure cubic zirconia (fully stabilized) or a mixture of cubic, monoclinic, and tetragonal zirconia (partially stabilized)[17–19]. Monoclinic and tetragonal zirconia, in contrast to cubic zirconia, exhibit predominantly electronic conduction[16,20]. Hence, the equilibrium phase composition (ratio of monoclinic and tetragonal zirconia to cubic zirconia) has a pronounced influence on the electrical characteristics of the electrolyte, and consequently on the e.m.f. response of the oxygen probe. The presence of impurities such as Al_2O_3, SiO_2, TiO_2, and Fe_2O_3 significantly increases the electronic conductivity of the solid electrolyte, resulting in a higher P_e value[11,13]. The P_e value is also influenced by the microstructure of the electrolyte. Segregated impurities, for example, increase the ratio of electronic to ionic conductivity, thus increasing the P_e value. High-purity, fully stabilized zirconia is therefore preferred in order to reduce the possibility of polarization and to ensure that stable e.m.f. readings are obtained. Unfortunately, the resistance to thermal shock of high-purity, fully stabilized zirconia is inadequate[17,18,21,22], and partially stabilized zirconia is utilized instead in commercial oxygen probes.

Whereas the equilibrium phase composition of a solid electrolyte at the measuring temperature is determined by the chemical composition, the initial phase distribution can be varied by control of the heat-treatment during manufacture. If the initial phase composition is different from that under equilibrium conditions, phase changes will occur when the probe is heated in the course of
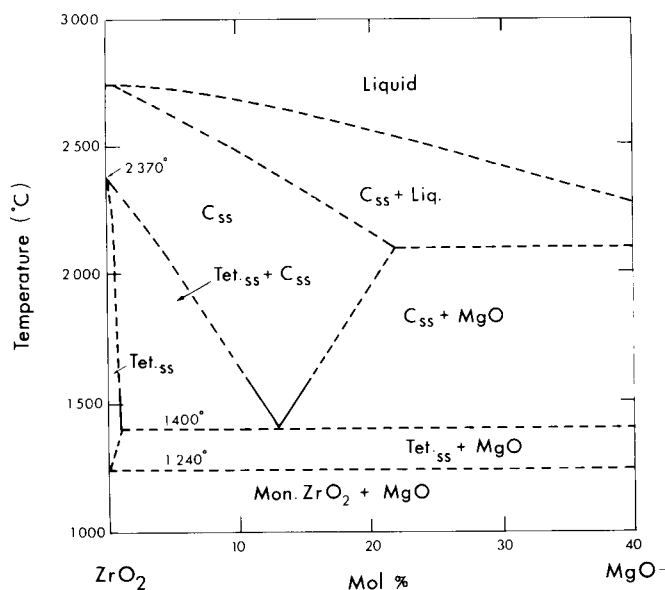

Fig. 4—Phase diagram of the ZrO₂–MgO system[31]
C_{ss} = Cubic solid solution
$Tet._{ss}$ = Tetragonal solid solution
Mon. = Monoclinic

oxygen activity measurements[6,23]. Fig. 5, taken from the work of Nakamura and Moriya[6], shows the change in volume fraction of cubic zirconia in 8,1 mole per cent magnesia-stabilized zirconia during measurements in liquid steel. The fraction of cubic zirconia increases immediately after immersion in the liquid steel until it reaches an equilibrium content of approximately 80 per cent. However, the rate of increase is dependent on the initial fraction of cubic zirconia, as shown for four different cases. For example, an electrolyte initially containing no cubic phase, will contain only 10 per cent cubic zirconia 10 seconds after immersion in the steel bath. Such partially stabilized zirconia can function as a solid electrolyte only if a sufficient amount of cubic zirconia is present, since monoclinic and tetragonal zirconia show virtually no ionic conduction. Consequently, a solid electrolyte containing only a small fraction of cubic phase will show poor e.m.f. response characteristics. This conclusion was confirmed experimentally by Nakamura and Moriya[6], who showed that the e.m.f. response of a magnesia-stabilized zirconia that initially did not contain any cubic phase was poor and did not attain a stable e.m.f. plateau during the first 10 seconds of immersion. This observation clearly demonstrates that the e.m.f. response of an oxygen probe is affected by the initial amount of cubic phase present in the solid electrolyte, and that the response improves with an increase in the fraction of cubic phase contained. They also showed that a good e.m.f. response is obtained when the initial amount of cubic phase contained in the solid electrolyte is approximately 27 per cent[6].

A clear picture emerges from a consideration of the available literature and recent experimental findings[7,13,24,25]. For the accurate determination of oxygen activity in liquid steel, the e.m.f. response curve of the oxygen probe should have a well-established, stable e.m.f. plateau, a short response time, and good reproducibility. The e.m.f. response is in large measure determined by the initial and
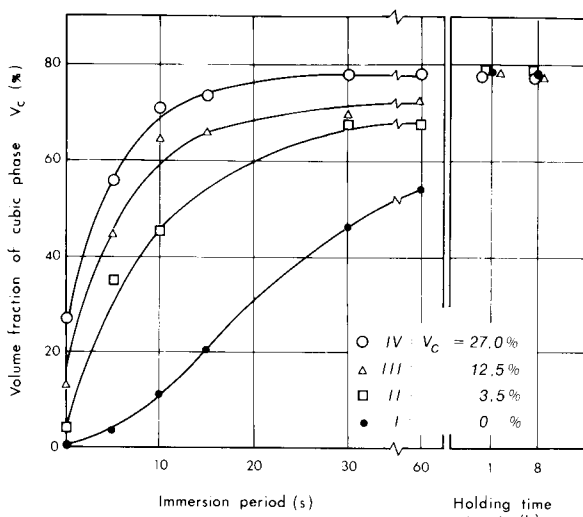
Fig. 5—Changes in volume fraction of cubic zirconia in an 8,1 mole per cent magnesia-stabilized zirconia when immersed in liquid steel at 1600°C, or when held in air at 1600°C for 1 and 8 hours[6]

equilibrium phase composition of the solid electrolyte, and strict control of the chemical and phase compositions, as well as of the microstructure of the solid electrolyte, is a necessary prerequisite for accurate and reproducible measurements. It was these considerations that led to the experimental investigation to finally prove this premise.

Although investigations as to the reliability of commercial oxygen probes have been conducted locally, they have usually been restricted to an evaluation of the data provided by the commercial signal-processing unit supplied with the probe[26]. The approach taken in the present investigation is different in the sense that the e.m.f. and temperature response signals from the probe were evaluated separately and subsequently correlated with the data obtained from the processing unit.

Experimental Investigation

Industrial trials were conducted in a vacuum degassing unit of The Union Steel Corporation located at their Vaal Works in Vereeniging. The oxygen content of liquid steel was measured by means of electrochemical oxygen probes in 50 t ladles for a variety of steel compositions.
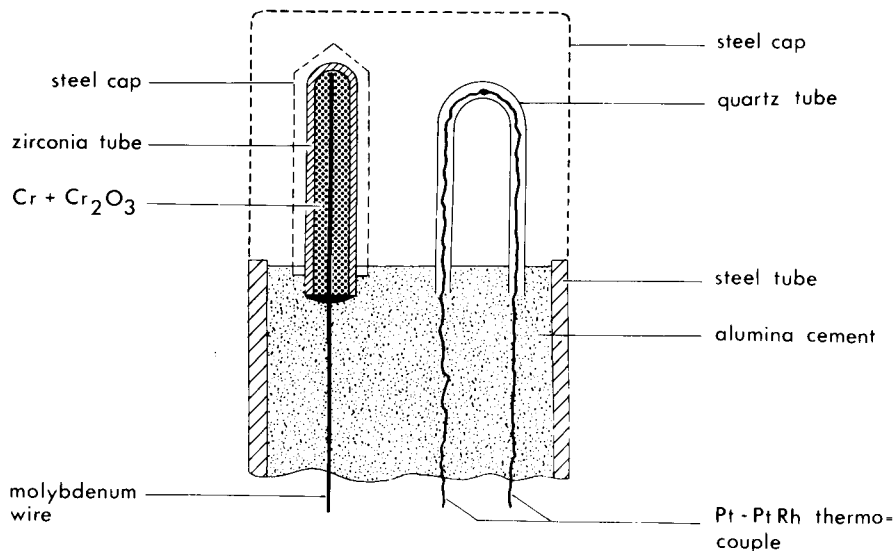
The design of the commercial oxygen probe used in this investigation is shown in the schematic diagram of Fig. 6. The electrochemical cell arrangement consists of a magnesia-stabilized zirconia solid electrolyte, a (Cr + Cr_2O_3) reference electrode, and a steel bath. A molybdenum wire inserted into the zirconia tube serves as the electrical lead to the reference electrode, while a steel tube surrounding the cell assembly is used as the electrical lead to the steel bath. The sensor is also equipped with a Pt–PtRh thermocouple contained inside a quartz protection tube. A steel cap protects both the electrolyte tube and the thermocouple. To complete the oxygen probe, the sensor is attached to an expendable cardboard tube. The detachable probe is mounted onto a lance, which is connected electrically to a signal-processing unit. Signals of cell potential and thermoelectric voltage are obtained simultaneously from the probe. When these signals attain stability, they are processed to provide a display and a hard printed copy of the temperature and of the dissolved oxygen content of the steel bath. When unstable e.m.f. temperature signals are experienced, the processing unit displays a no-reading sign[27]. In the present investigation, the signal-processing unit was coupled in parallel to a two-pen recorder, allowing simultaneous recording of the e.m.f. and temperature response curves.

Oxygen measurements were taken by the immersion of a probe, mounted on a hand-held lance, in the liquid steel to a depth of 0,3 to 0,4 m below the slag layer. Since the steel temperatures were usually above 1600°C, the immersion time was limited to 9 seconds. Both single and successive oxygen measurements were made. Successive measurements were made at 45-second intervals. The measurements obtained from the processing unit were correlated with the recorded e.m.f. and temperature response curves, and were used for further evaluation. Since excellent results were obtained with the temperature response signals (an average response time of 2 seconds and an uncertainty in temperature of $\pm 3°C$[7]), only the e.m.f. response curves are considered in the following discussion.

In an investigation of the consistency of the electrical and physical properties of the electrolytes used in commercial oxygen probes, several electrolytes from different batches of probes were submitted for chemical analysis,

Fig. 6—Schematic diagram showing the construction of the commercial oxygen probe

X-ray-diffraction analysis, scanning electron microscopy, and microprobe X-ray analysis. The chemical composition of the electrolytes was determined by inductively coupled plasma emission spectroscopy. The degree of stabilization, i.e. the volume fraction of cubic zirconia in the electrolyte, was estimated by means of an X-ray powder-diffraction technique[6,11,28]. For the preparation of the sample powders, the electrolytes were crushed and ground to minus 325 mesh, during which the tetragonal zirconia contained in the electrolyte was transformed to monoclinic symmetry[6,29]. The phase analysis was made from a determination of the ratio of the diffraction intensities of the cubic and monoclinic zirconia, as given by equation (4):

$$X = \frac{I_c(111)}{I_m(11\bar{1}) + I_c(111)}, \quad \dotfill (4)$$

where $I_c(111)$ and $I_m(11\bar{1})$ denote the peak heights of the diffraction patterns of the (111) plane of cubic zirconia and the $(11\bar{1})$ plane of monoclinic zirconia respectively. The intensity ratios so obtained were converted to the volume fraction of cubic zirconia by means of the calibration curve given by Nakamura and Moriya[6].

Results and Discussion
Properties of the Solid Electrolyte
The chemical composition and degree of stabilization of the electrolytes from three different batches of oxygen probes are summarized in Table I. The microstructures of the electrolytes were studied by scanning electron microscopy and microprobe X-ray analysis, and typical examples of the microstructures are shown in Fig. 7.

Most commercially available zirconia-based solid electrolytes contain impurities, particularly silica and alumina[11,13]. The impurities can be added deliberately to control grain growth and aid densification during the sintering process, or can be introduced inadvertently via the original raw material. When present in relatively large concentrations, these impurities segregate to the grain boundaries and give rise to a lower ionic conductivity and a higher P_e value[11,13]. As shown in Table I, the chemical compositions of the electrolytes from different batches of oxygen probes were virtually the same, except for the silica content, which varied slightly. The silica and magnesium oxide distributions in the electrolytes are shown in Figs. 7(c) to (f) as the silicon and magnesium distributions derived from microprobe X-ray analysis. The white areas in Figs. 7(e) and 7(f) represent high concentrations of silicon, and indicate that the silica content of these electrolytes was not low enough to avoid segregation of the silica. However, it is important to note that the amount

of segregation in the different electrolytes was approximately the same. Iwase et al.[11] and Van Wijngaarden[13] have shown that, as long as the microstructure of different electrolytes remains the same, small variations in the silica content ($\pm$ 0,5 per cent) do not significantly affect the ionic conductivity or the P_e value of the electrolyte. This conclusion suggests that the small variation in silica content of the different electrolytes will not affect the electrical properties and, accordingly the e.m.f. response of the oxygen probe, significantly.

From the back-scattered electron images and the magnesium distribution shown in Fig. 7, it is evident that the microstructure of the electrolytes consists of relatively coarse-grained cubic zirconia rich in magnesium oxide, and finer-grained monoclinic zirconia lean in magnesium oxide. The monoclinic grains are believed to have been present during sintering, and were probably derived from tetragonal zirconia that had been in equilibrium with cubic zirconia at the sintering temperatures above 1400°C (Fig. 4: 5,9 mole per cent for these electrolytes). Table I shows that the degree of stabilization of the different electrolytes is very nearly the same, again suggesting that the e.m.f. response of the commercial oxygen probe will be reproducible. A quantitative assessment of the relationship between the microstructure and the electrical properties of these electrolytes is currently being pursued in a separate investigation[30]. Previous investigators have shown that the 23 to 25 per cent cubic zirconia that is present in the electrolytes used in this study should be sufficient to produce a rapid and stable e.m.f. response[6]. These previous findings, together with the results of the present investigation, indicate that accurate and reproducible oxygen measurements should be possible with the new commercial oxygen probes.

Industrial Trials
As shown in the previous discussion, the performance of an oxygen probe should be evaluated with reference to the e.m.f. response curve. Accordingly, all the e.m.f. response signals obtained in this investigation were evaluated with special reference to the stability of the e.m.f. response and the uncertainty in the absolute value of the e.m.f. measured. Typical examples of such e.m.f. response curves obtained during the industrial trials are shown in Fig. 8. These experimentally determined curves were classified as excellent, acceptable, or unacceptable, and typical examples of each classification are given in Fig. 8. A classification of excellent was assigned to a response curve showing a long, stable e.m.f. plateau with a small uncertainty in e.m.f. value. For an e.m.f. response curve to be classified as acceptable, it had to have at least

TABLE I

CHEMICAL COMPOSITION AND DEGREE OF STABILIZATION OF THE SOLID ELECTROLYTES USED IN THE COMMERCIAL OXYGEN PROBES

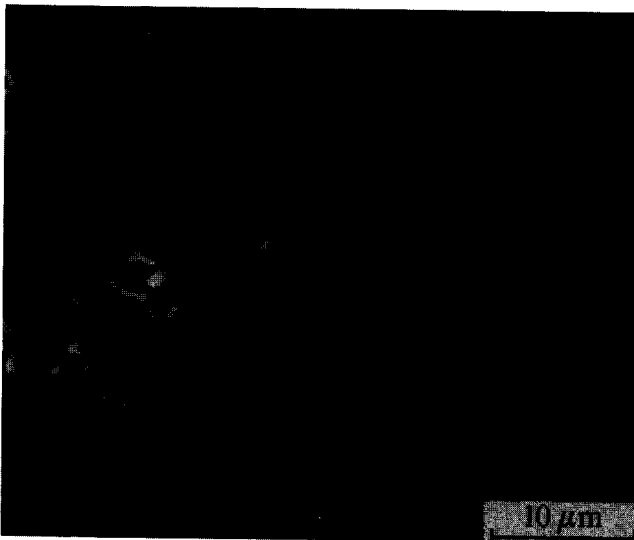| Batch no. | Chemical composition, % (by mass) | | | | | | | | Degree of stabilization % (by vol.) of cubic ZrO_2 |
	MgO	CaO	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	Na_2O	K_2O	
1	2,01	0,42	0,38	0,16	0,11	0,04	tr	tr	23
2	2,02	0,45	0,26	0,14	0,11	0,07	tr	tr	24
3	2,02	0,40	0,32	0,14	0,11	0,06	tr	tr	25

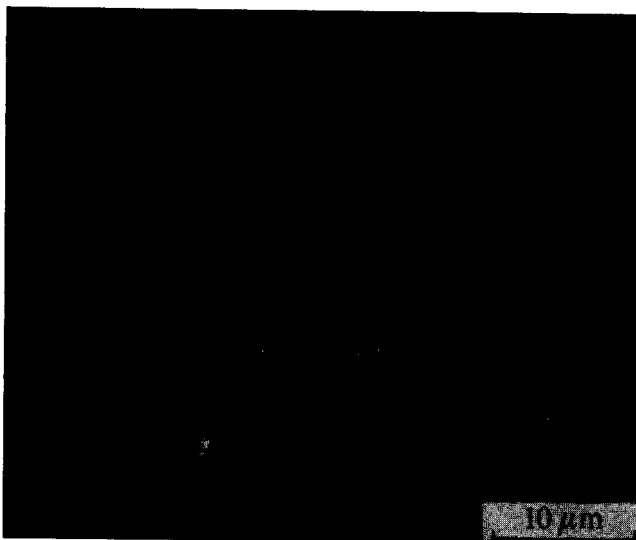tr = Trace
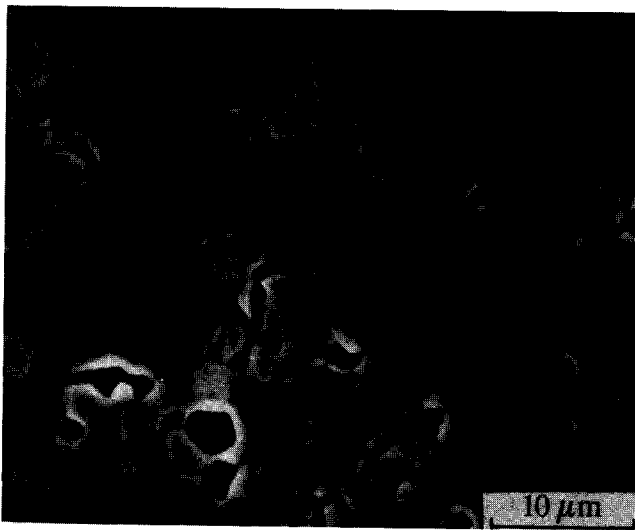
(a) Back-scattered electron image (Batch 1)
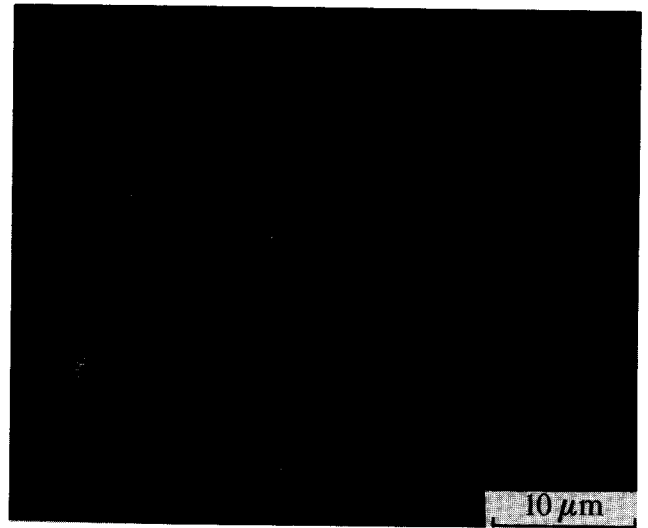
(d) Characteristic X-ray image, magnesium distribution (Batch 2)
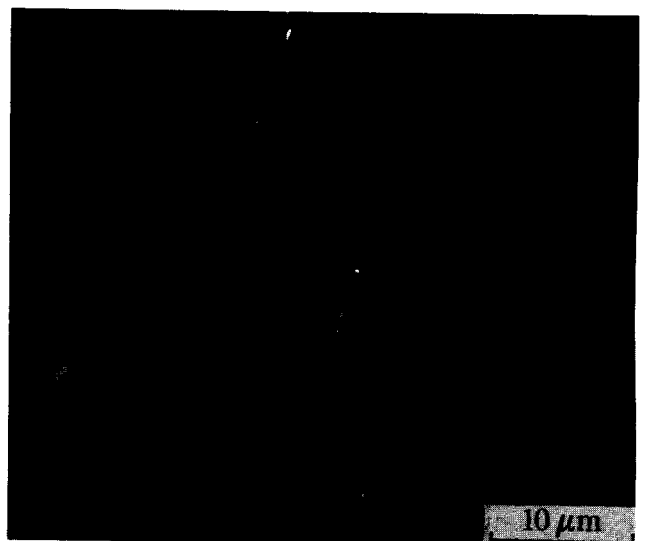

(b) Back-scattered electron image (Batch 2)

(e) Characteristic X-ray image, silicon distribution (Batch 1)

(c) Characteristic X-ray image, magnesium distribution (Batch 1)

(f) Characteristic X-ray image, silicon distribution (Batch 2)

Fig. 7—The microstructures of the solid electrolytes from two different batches of oxygen probes
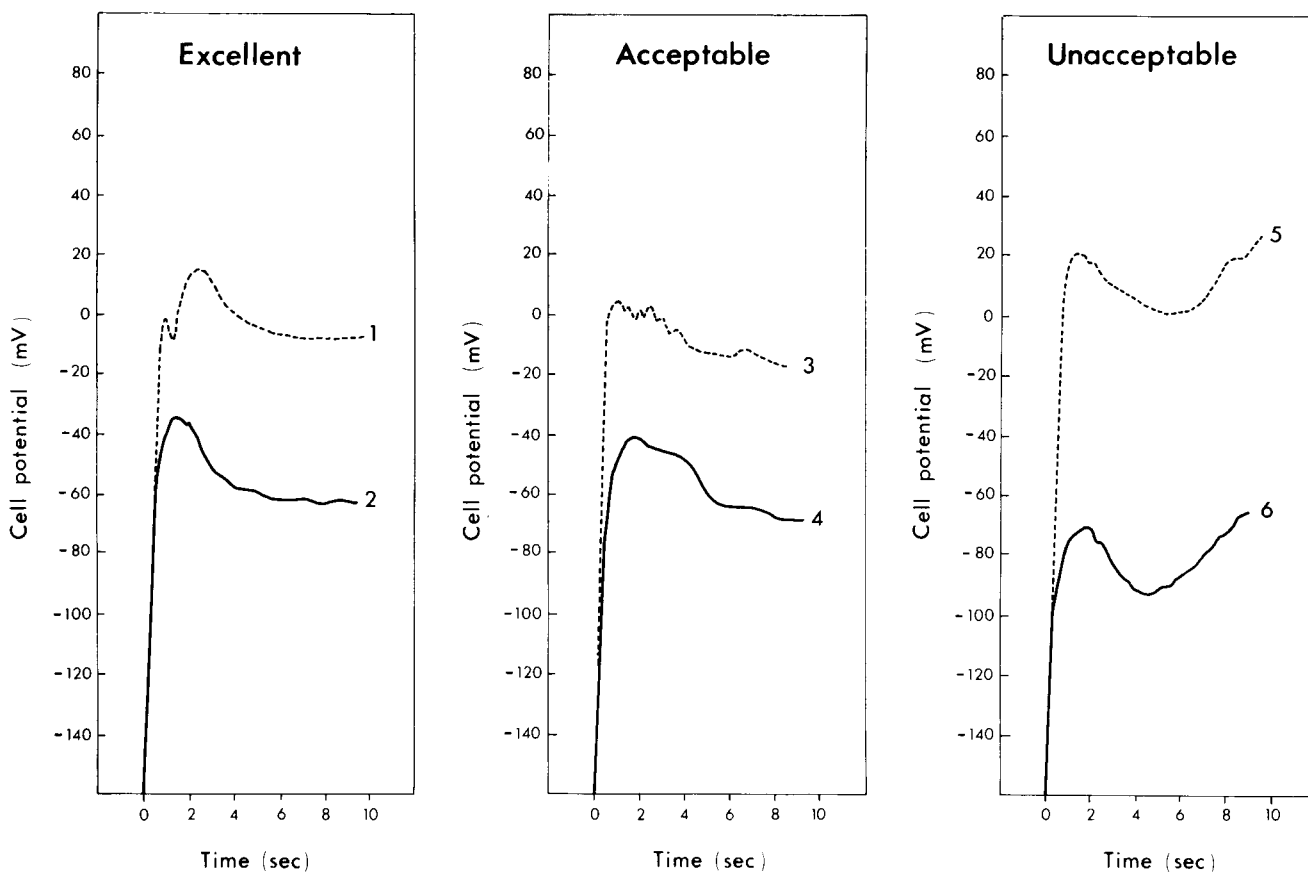
Fig. 8—Classification of the e.m.f. response curves obtained with the commercial oxygen probe during the industrial trials

a short e.m.f. plateau, but small fluctuations were acceptable. Since the absence of a stable e.m.f. plateau indicates that thermodynamic equilibrium was not attained in the reference electrode or in the solid electrolyte, the presence of an obvious plateau was considered a necessary prerequisite for an acceptable e.m.f. curve. Consequently, an e.m.f. curve could be regarded as stable but, if an obvious plateau was absent, the curve was classified as unacceptable. Clearly, this classification is somewhat arbitrary, but it does provide a means of comparison for the response performances of commercial oxygen probes.

The success rate obtained from the processing unit, as well as from the e.m.f. response curves, is summarized in Table II. It is evident that the number of successful measurements obtained from the processing unit (92 per cent) is higher than that obtained from the actual e.m.f. response curves (80 per cent). This can be explained with reference to curve 5 in Fig. 8. No obvious plateau is present in this case, but the e.m.f. continues to increase with time, and it is uncertain whether or not thermodynamic equilibrium has been attained. This curve was therefore classified as unacceptable. However, the curve shows relatively constant e.m.f. values after 6 and 8 seconds immersion time respectively, and the electronic brain of the processing unit would interpret this curve as stable[7] and read an e.m.f. value of either 2 mV or 19 mV. This implies that the processing unit will indeed in some cases give a reading, but that the indicated oxygen level could be erroneous. Thus, the accuracy of the reading would not be known in the absence of a recorded response curve.

It is also important to realize that the success rate depends very much on the physical handling of the probe. For example, several of the measurements that were classified as unacceptable in the early stages of the investigation could be traced back to improper handling of the probe. The plant operators were more familiar with the probe by the end of the investigation, and the achievement rate obtained from interpretation of the e.m.f. response curve increased to approximately 90 per cent simply because the probe was handled properly. It is therefore recommended that, whenever possible, the probe should be mounted on a mechanical lance so that measurements can be made automatically. In this way, buoyancy forces and vibration would be eliminated, and successive measurements would always be made to the same depth in the liquid steel.

The reproducibility of the oxygen measurements was determined from three successive dip tests within a short

TABLE II

SUCCESS RATE OF OXYGEN MEASUREMENTS UNDER PLANT CONDITIONS

No. of measurements	Success rate		
	Processing unit	e.m.f. response curve	
	Excellent	Acceptable	Unacceptable
100	92 45	35	20

Fig. 9—Examples of the e.m.f. response curves of three successive oxygen measurements

$$\frac{d[\%(O)]}{\%(O)} = d[\ln \%(O)] = 2,3 \, d[\log \%(O)] = 2,3$$
$$d(1,36 + 0,0059 \, [E + 0,54 \, (T\text{-}1550) + 2\cdot10^{-4} \, E \, (T\text{-}1550)]) \leq 9,376\cdot10^{-3} \, |dE| + 7,336\cdot10^{-3} \, |dT| + 2,717\cdot10^{-6} \, (|E| \, |dT| + |T| \, |dE|), \quad\quad\quad\quad\quad (5)$$

where $|dE|$ and $|dT|$ denote the absolute values of the uncertainty in e.m.f. plateau (mV) and the uncertainty in temperature respectively. The uncertainty in temperature was taken as $\pm$ 3°C (average uncertainty of all the temperature measurements[7]). The uncertainty in oxygen concentration of the individual measurements is summarized in Table III.

From the results reported in Table III, it is evident that the oxygen concentrations calculated from the e.m.f. response curves are in good agreement with those obtained from the processing unit and that the reproducibility in the measurement of oxygen concentration is good. On the basis of these results, a good measure of confidence can be placed in the ability of the new commercial oxygen probe to accurately measure the dissolved oxygen content of liquid steel. However, the accuracy of equation (4) was not confirmed in the present study but is the subject of a separate investigation[30].

Conclusions

(1) Accurate and reproducible measurements of oxygen in liquid steel can be made with commercial oxygen probes only if the chemical and phase compositions, and the microstructure of the solid electrolytes contained in various batches, do not vary significantly.

(2) The dissolved oxygen content of liquid steel was measured correctly and with good reproducibility by the commercial oxygen probe evaluated in this investigation.

(3) The number of successful measurements and the reliability of the e.m.f. response of the probe depends on proper handling of the probe. The probe should preferably be immersed automatically by means of a mechanical lance.

(4) The signal processing unit supplied with the oxygen probe is able to interpret the e.m.f. signal accurately. Nevertheless, the possibility exists that the processing unit will accept e.m.f. signals even in the absence of a well-established e.m.f. plateau, and it is recommended that a permanent record of the temperature and e.m.f. response curves should be kept and evaluated separately for each oxygen measurement.

(5) The data provided by the processing unit can be used to control the degree of oxidation of the steel provided the measurement is based on a well-established plateau of the e.m.f. response curve.

period of time in the same bath. An example of the e.m.f. response curves of three such successive oxygen measurements is given in Fig. 9, and the results obtained in this part of the investigation are summarized in Table III.

In a determination of whether the e.m.f. response curve was being interpreted correctly by the processing unit, the oxygen concentrations obtained from the unit were compared with the oxygen concentrations calculated from the e.m.f. plateaus of the recorded e.m.f. response curves. The calibration curve used electronically by the processing unit to calculate the oxygen content of the steel is given by the following formula:

$$\log \%(O) = 1,36 + 0,0059 \, [E + 0,54 \, (T\text{-}1550) + 2\cdot10^{-4} \, E \, (T\text{-}1550)] \quad\quad\quad\quad\quad (4)$$

where E and T denote the cell potential (mV) and temperature (°C) respectively.

In the interpretation of the e.m.f. response curves, it was assumed that equation (4) is valid, and this formula was used in the calculation of the oxygen content from the e.m.f. plateau. Whereas the processing unit displays only a single oxygen concentration, the e.m.f. response curve can be analysed to give the average oxygen concentration, as well as the uncertainty in oxygen concentration. The uncertainty in the measured value of oxygen concentration was calculated from the equation

TABLE III
REPRODUCIBILITY OF SUCCESSIVE OXYGEN MEASUREMENTS UNDER INDUSTRIAL CONDITIONS

No.	Temperature °C	Obtained from processing unit, p.p.m.			Obtained from e.m.f. response curve, p.p.m.		
		Measured	Average	Std deviation	Measured	Average	Std deviation
1.1	1642	18,5			18,3 ± 1,2		
1.2	1639	19,5	19,0	0,5	18,9 ± 0,9	18,5	0,3
1.3	1638	19,1		.	18,3 ± 1,2		
2.1	1614	15,5			16,0 ± 0,8		
2.2	1614	15,4	15,3	0,3	Unacceptable e.m.f.	15,1	1,3
2.3	1614	14,9			14,2 ± 1,1		
3.1	1682	55,8			55,5 ± 2,8		
3.2	1683	56,0	58,3	4,2	55,9 ± 2,0	58,6	5,0
3.3	1683	63,2			64,3 ± 2,3		
4.1	1625	10,0			9,9 ± 0,6		
4.2	1624	10,6	10,5	0,4	10,5 ± 0,5	10,4	0,4
4.3	1623	10,8			10,7 ± 0,5		
5.1	1715	55,1			53,4 ± 2,7		
5.2	1715	58,2	57,3	2,0	53,4 ± 2,7	53,8	0,6
5.3	1715	58,7			54,5 ± 3,1		
6.1	1592	6,9			6,8 ± 0,2		
6.2	1593	8,8	8,1	1,0	8,8 ± 0,3	8,0	1,1
6.3	1591	8,5			8,4 ± 0,4		
7.1	1734	49,0			49,9 ± 2,9		
7.2	1732	52,5	51,1	1,8	51,4 ± 2,2	50,5	0,8
7.3	1726	51,7			50,2 ± 2,5		
8.1	1707	82,0			78,8 ± 6,2		
8.2	1705	84,4	84,1	2,0	84,5 ± 3,1	83,7	4,5
8.3	1706	86,0			87,7 ± 4,4		
9.1	1586	3,0			Unacceptable e.m.f.		
9.2	1587	3,6	3,5	0,4	3,8 ± 0,1	3,8	0,0
9.3	1586	3,8			3,8 ± 0,2		
10.1	1635	6,7			6,9 ± 0,3		
10.2	1639	No reading	8,5	2,5	8,4 ± 0,5	7,7	1,1
10.3	1635	10,3			Unacceptable e.m.f.		

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