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Automatic titration of reducing gases in inert gases using an oxygen pump-gauge

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A computer-aided gas analyzing system with a zirconia oxygen pump-gauge was developed and used to measure a small amount of reducing gas in a flowing inert gas. The flowing Ar containing CO or CH_4 was automatically titrated with oxygen by scanning the current of the oxygen pump; on-line titration data were analyzed by correcting for the response delay of the EMF sensor to the pump current. This scan method is very advantageous for a precise and rapid determination of the total oxygen demand (TOD) of the flowing gas.

1. Introduction

Oxygen concentration cells with stabilized zirconia electrolytes are utilized as devices for monitoring or controlling oxygen quantities in gases at high temperatures [1].

A zirconia oxygen pump-gauge, comprising an oxygen pump and sensor components, enables the titration of a reducing gas in inert gases. In our previous paper [2], flowing gases containing a small amount of CO in Ar were titrated with oxygen with a zirconia oxygen pump-gauge and CO quantities were precisely determined by analyzing the steady-state titration curves. However, it was wasteful of time for the measuring system to reach a new steady state after a current change in the oxygen pump. Consequently, it took a long time to obtain a series of steady-state titrated values. In addition, it was not easy to maintain the strict experimental conditions during such a long run. Alternatively, if titration curves for the reducing gas can be obtained by scanning the pump current over a short time, then this will offer a more powerful method for analyzing the quantities of reducing gas.

In this paper, a computer-aided automatic analyzing system for a small amount of CO or CH_4 in Ar is described. The analysis of the titration curves by the scan method is discussed on the basis of the response equation. The results obtained are compared to those obtained from the steady-state method.

2. Experimental details

The detail of the oxygen pump-gauge used in this study was described in a previous paper [2]. Briefly, it consisted of a pump with Pt electrodes 40 mm wide, and a sensor with Pt electrodes 5 mm wide sectioned in a $0.92ZrO_2 \cdot 0.08Y_2O_3$ tube with an inner diameter of 9 mm. The centre of the pump was separated by 235 mm from that of the sensor in order to prevent mutual electrical interference. Each component (pump and sensor) was heated independently by a furnace with a non-inductive winding. This assembly was different from the three-electrode assembly used by Yuan and Kröger [3] and from the four-electrode assembly of Agrawal *et al.* [4] which was housed in a common furnace.

The block diagram of the automatic measuring system is shown in Fig. 1. The applied current of the oxygen pump was swept with a triangular wave form by a function generator through a galvanostat. Recording of the variation with time of the applied current of the oxygen pump and the EMF of the oxygen sensor to analyze the reducing gas was carried out via an on-line computer. The flow diagram for the computer-control program is shown in Fig. 2. If, instead, a function generator operated through a bus interface was used, then the program would be shorter.

Mixtures of Ar-2.10 × 10^{-2} % CO and Ar-4.76 × 10^{-3} % CH_4 were used as the sample gases. The concentrations of CO and CH_4 were determined by gas chromatography. The flow rate of the gas was controlled by a mass-flow controller and it was measured with a soap film flow-meter attached to the gas outlet of the oxygen pump-gauge. Both the pump and the sensor were operated at 973 K throughout.

3. Principle of the method

Consider an inert gas containing a small quantity of a reducing component, R, x moles of which react stoichiometrically with 1 mole of oxygen to produce stable oxide. When R is CO, $x = 2$ and the reaction is $2CO + O_2 = 2CO_2$, and when R is CH_4, $x = \frac{1}{2}$ and the reaction is $\frac{1}{2}CH_4 + O_2 = \frac{1}{2}CO_2 + H_2O$. The mixture flowing at a mass-flow rate V (mol s^{-1}) under a total pressure $P_T (= 1.013 \times 10^5$ Pa) reacts with a sufficient oxygen, supplied by the oxygen pump, to completely burn the reducing gas and to maintain a condition of excess oxygen. If the quantities of R and pumped-in oxygen are so small that the volume

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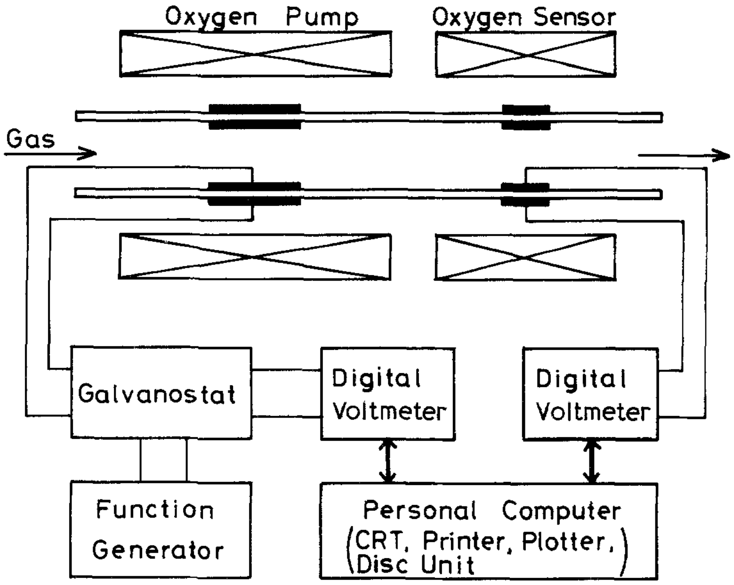

Fig. 1. Block diagram of the automatic measuring system.

change of the gas mixture by the reaction can be ignored, then the oxygen partial pressure P_{O_2} (Pa) measured in the steady state after the reaction is given by

$$\frac{P_{O_2}}{P_T} = -\frac{P_R^0}{xP_T} + \frac{m}{V} + \frac{I}{4FV} \quad (1)$$

where P_R^0 is the partial presure of R, I the applied current of the oxygen pump, F the Faraday constant, and m the mass-flow rate for oxygen leaking from the surroundings into the measuring system. The oxygen leakage results from the slightly imperfect air-tightness of the system and the semipermeability of the zirconia solid electrolyte, for which the latter is predominant above 1100 K [5]. To decrease the oxygen leakage from the zirconia tube, both the temperatures of the pump and the sensor were operated at 973 K in this study. The leak rate of oxygen, which was obtained as the slope of Equation 1 by plotting P_{O_2}/P_T against V^{-1} in the condition that $P_R^0 = 0$ and $I = 0$, was found to be 5.71×10^{-11} mol s^{-1}. The value of m/V at a typical mass-flow rate of 5×10^{-5} mol s^{-1} was 1.16×10^{-6}, which is negligibly small in comparison with P_R^0/xP_T for the used gases. Plots of P_{O_2}/P_T against I at constant flow rate give a straight line, and the negative value of the intercept on the P_{O_2}/P_T axis shows the total oxygen demand (TOD). TOD is defined as the minimum quantity of oxygen necessary for completely burning the gas: the value being positive for a reducing gas and negative for an oxidizing gas. The fraction of the reducing component, P_R^0/P_T is calculated from x times TOD. In the previous paper

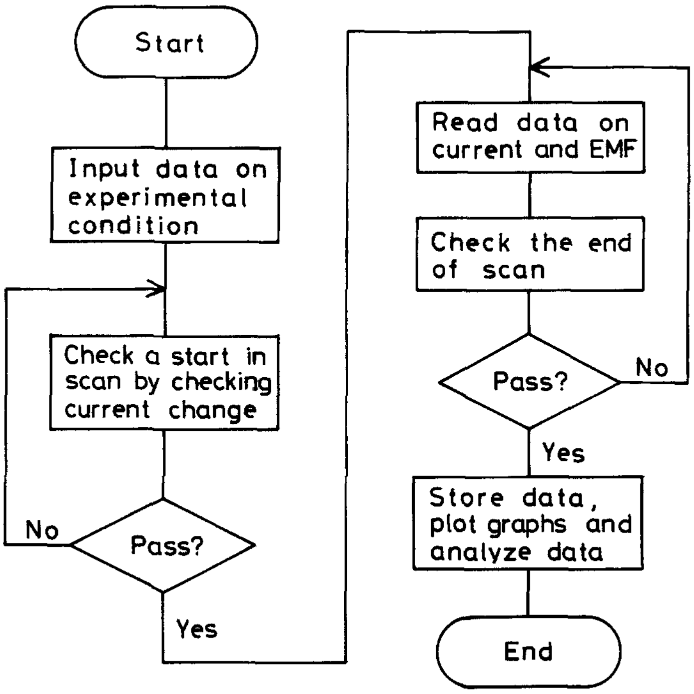

Fig. 2. Flow diagram for the computer program.

[2], Equation 1 was found to hold strictly in the case of R being CO. Further, upon putting $P_{O_2} = 0$ and $m = 0$ in Equation 1, the current at the equivalence point of the reaction, I_{eq} is given by

$$I_{eq} = \frac{4FV}{x}\left(\frac{P_R^0}{P_T}\right). \quad (2)$$

At the equivalence point a drastic change of oxygen partial pressure occurs. Therefore, if I_{eq} is measured directly at the equivalence point, then the fraction of the reducing gas may also be calculated from Equation 2. Unfortunately, it is not easy to determine I_{eq} precisely by this method. Around the equivalence point the oxygen partial pressure is unstable because the buffer capacity of the gas against oxygen reaches its lowest value [2]. Therefore, the use of Equation 1 is preferable to the use of Equation 2 for the precise analysis of the reducing gas. But when the current of the oxygen pump is swept with time, Equation 1 is not entirely valid because of the delay of the response of the sensor to the current change in the pump. This extra difficulty is discussed below.

4. Results and discussion

4.1. *Response time of the oxygen pump-gauge*

When the sensor does not respond promptly to the current applied by the scan method, it is necessary to consider the effect of the delay of the response on the titration curve.

As shown in Fig. 1, the sensor is separated from the pump in order to prevent mutual electrical interference. As a result it takes a certain time for a flowing mixture to arrive at the sensor from the pump. If the gas were transferred in the tube with simple plug and diffusional flow, the delay due to the gas flow could be calculated by Fick's diffusion law [6]. However, the actual gas flow in the oxygen pump-gauge is considered to be very complex. A turbulent flow in the zirconia tube occurs due to the Pt gauges and lead wires attached to the Pt paste electrodes in both pump and the sensor. Furthermore, a flowing gas expands or contracts corresponding to the temperature distribution of the oxygen pump-gauge. There is also a delay due to the mass transfer and reaction of the gaseous components at the porous electrodes of the pump and the sensor which should be considered [7–10]. Therefore, the actual response time is treated as an apparatus constant under given measuring conditions.

The mean residence time, τ, which is analyzed from the output signal at the sensor in response to a step input signal at the pump [11], is a good measure of the response time. When the applied current is changed from a constant value followed by a current step, the measured oxygen pressure at the sensor is changed from an initial value $P_{O_2}(\mathrm{I})$ to $P_{O_2}(\mathrm{II})$. The difference in the total mass of oxygen flowing in and flowing out of the oxygen pump-gauge until the measured oxygen pressure at the sensor reaches $P_{O_2}(\mathrm{II})$ is given as

$$\int_0^\infty V\left(\frac{P_{O_2}(\mathrm{II})}{P_T} - \frac{P_{O_2}}{P_T}\right) \mathrm{d}t.$$

If the output signal is assumed to change stepwise with the time lag, τ, this incremental difference is

$$V\left(\frac{P_{O_2}(\mathrm{II})}{P_T} - \frac{P_{O_2}(\mathrm{I})}{P_T}\right)\tau.$$

Therefore, the mean residence time is given by

$$\tau = \int_0^\infty \frac{P_{O_2}(\mathrm{II}) - P_{O_2}}{P_{O_2}(\mathrm{II}) - P_{O_2}(\mathrm{I})} \mathrm{d}t. \quad (3)$$

Figure 3 shows the response of the sensor to current steps at the pump. The measured oxygen partial pressure did not change for about 4 s. This 'dead time' was proportional to the reciprocal flow rate of the measuring gas. The oxygen partial pressure then changed to

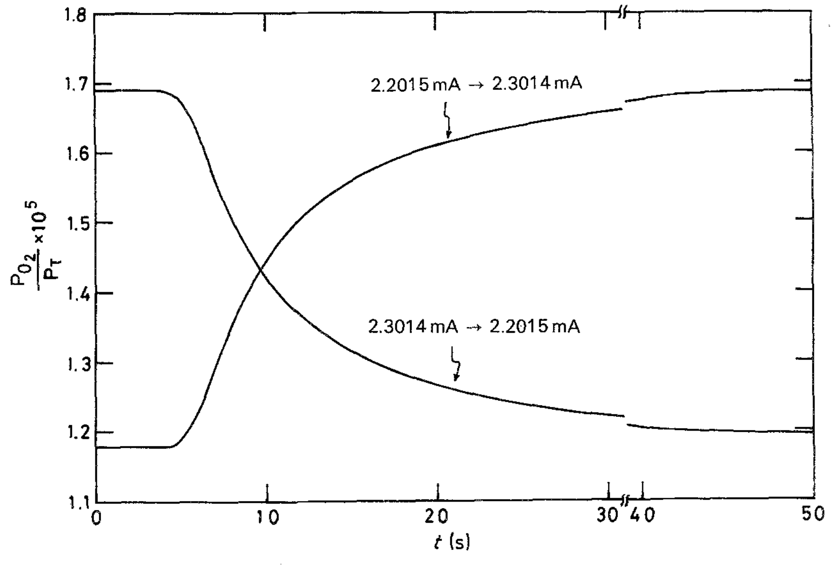

Fig. 3. Variation of oxygen partial pressure in Ar-2.10 × 10^{-2}% CO at a mass-flow rate of 5.07 × 10^{-5} mol s^{-1} with time resulting from current steps at $t = 0$ from 2.2015 to 2.3014 mA and *vice versa*.

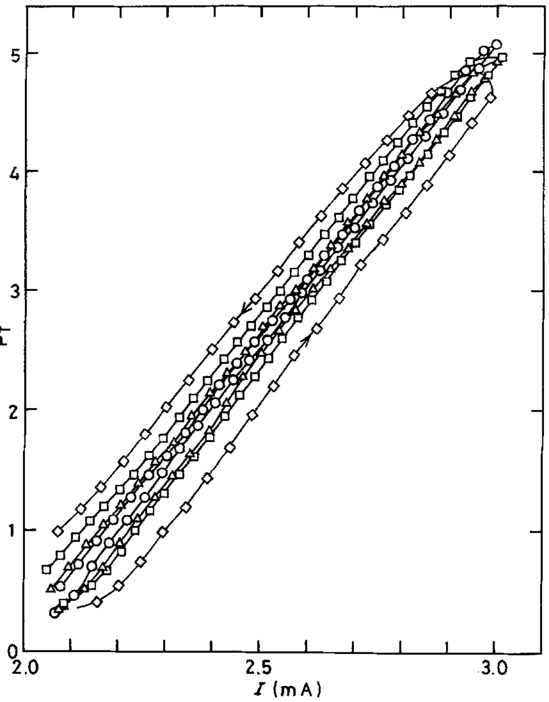

Fig. 4. Variation of oxygen partial pressure in Ar–2.10 × 10^{-2}% CO with pump current at various scan rates and a mass-flow rate of 5.04 × 10^{-5} mol s^{-1}. (○) 8.333 × 10^{-4} mA s^{-1}, (△) 1.667 × 10^{-3} mA s^{-1}, (□) 3.333 × 10^{-3} mA s^{-1}, (◇) 6.667 × 10^{-3} mA s^{-1}.

reach a steady-state value. A steady-state was obtained after 50 s. The value of τ obtained by integrating the curves in Fig. 3, using Equation 3, was 12.8 s in the upward step and 12.9 s in the downward step. This coincidence shows that the measured τ may be treated as the apparatus constant under constant measuring conditions. Otherwise the measured τ decreased with increasing gas flow rate and pump and sensor temperatures.

4.2. *Effect of the scan rate*

The scan rate of the pump current affects the automatic titration curve because of the response delay inherent in the apparatus.

Figure 4 shows the effect of the scan rate on the titration curve for the Ar–2.10 × 10^{-2} % CO mixture. Figure 5 shows the result for the Ar–4.76 × 10^{-3} % CH_4 mixture. The pump current was scanned with triangular wave forms. Hystereses in the titration curves were observed. The oxygen partial pressure varied linearly with the current except for the early stages of current increase and decrease. The deviation between the lines in the forward and reverse scans increased with scan rate. This phenomenon is analyzed below.

Consider that the pump current I(A) changes from a constant value following a ramp function of time. The initial current is I_0(A) and the sweep rate is α(A s^{-1}). When after a certain time, the state of the system changes while maintaining a pseudo steady state corresponding to the current change, the response of the sensor to the pump will be delayed by the mean residence time τ. Hence, at time t, the oxygen partial pressure corresponding to a current of $I_0 + \alpha(t - \tau)$ will be measured at the sensor. Consequently, Equation 1 is modified to become

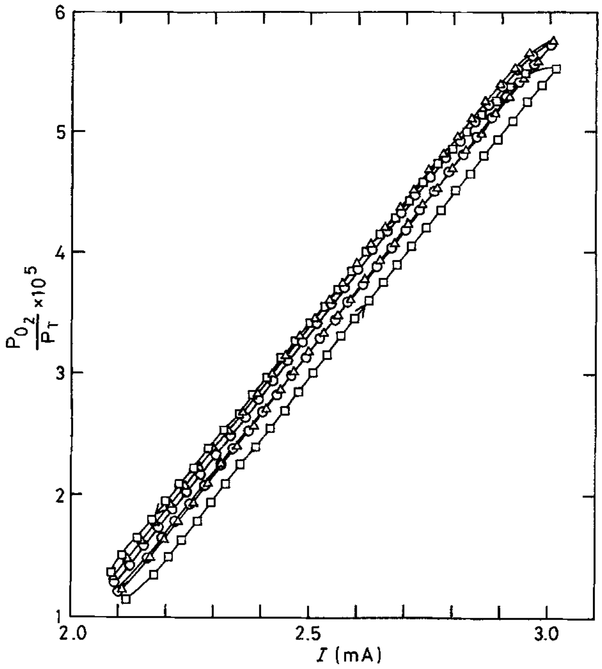

Fig. 5. Variation of oxygen partial presure in Ar-4.76 × 10^{-3}% CH_4 with pump current at various scan rates and a mass-flow rate of 5.20 × 10^{-5} mol s^{-1}. Symbols as in Fig. 4.

$$\begin{aligned}\frac{P_{O_2}}{P_T} &= -\frac{P_R^0}{xP_T} + \frac{I_0 + \alpha(t-\tau)}{4FV}\\ &= -\frac{P_R^0}{xP_T} + \frac{I}{4FV} - \frac{\alpha\tau}{4FV}. \qquad (4)\end{aligned}$$

The oxygen partial pressures $P_{O_2}(+)$ measured at a sweep rate of α (forward scan) and $P_{O_2}(-)$ at a sweep rate of $-\alpha$ (reverse scan) are represented by

$$\frac{P_{O_2}(+)}{P_T} = -\frac{P_R^0}{xP_T} + \frac{I}{4FV} - \frac{\alpha\tau}{4FV}$$

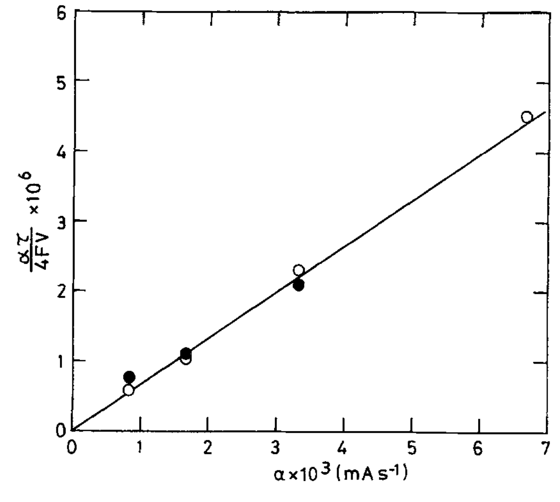

Fig. 6. Confirmation of Equation 4. Values of $\alpha\tau/4FV$ are obtained as halves of deviations between lines in increasing and decreasing current shown in Figs 4 and 5. The solid line shows that calculated when τ = 12.9 s and V = 5.07 × 10^{-5} mol s^{-1}. (○) Ar-2.10 × 10^{-2}% CO, (●) Ar-4.76 × 10^{-3}% CH_4.

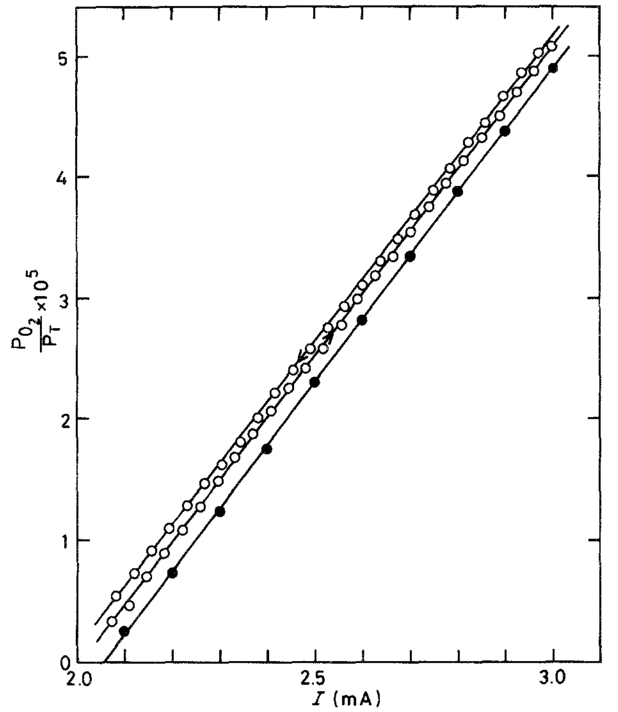

Fig. 7. Variation of oxygen partial pressure in Ar-2.10 × 10^{-2}% CO with pump current by the (●) steady-state (mass-flow rate 5.14 × 10^{-5} mol s^{-1}) and (○) scan methods (scan rate 8.333 × 10^{-5} mA s^{-1}, mass-flow rate 5.04 × 10^{-5} mol s^{-1}).

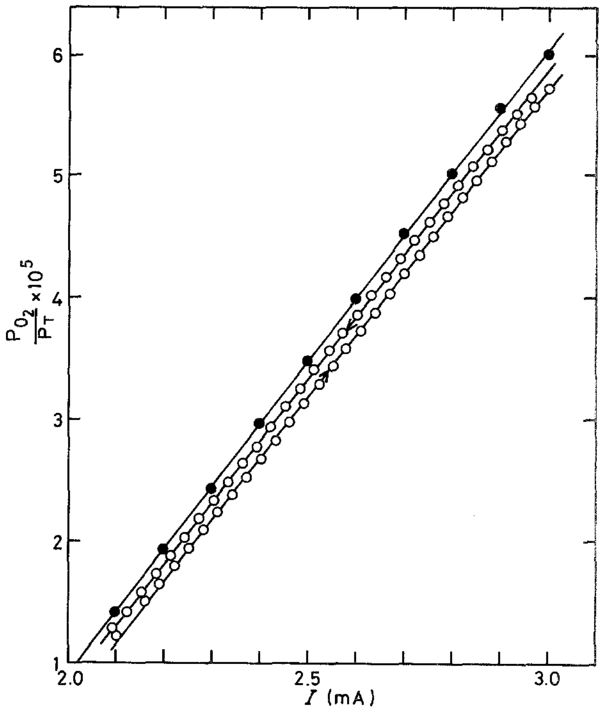

Fig. 8. Variation of oxygen partial pressure in Ar-4.76 × 10^{-3}% CH_4 with pump current by the (●) steady-state (mass-flow rate 5.22 × 10^{-5} mol s^{-1}) and (○) scan methods (scan rate 8.333 × 10^{-4} mA s^{-1}, mass-flow rate 5.20 × 10^{-5} mol s^{-1}).

and

$$\frac{P_{O_2}(-)}{P_T} = -\frac{P_R^0}{xP_T} + \frac{I}{4FV} + \frac{\alpha\tau}{4FV}.$$

Therefore, the relation

$$\frac{1}{2}\left(\frac{P_{O_2}(+) + P_{O_2}(-)}{P_T}\right) = -\frac{P_R^0}{xP_T} + \frac{I}{4FV} \qquad (5)$$

is obtained. Further, τ is given by

$$\tau = \frac{2FV}{\alpha}\left(\frac{P_{O_2}(-) - P_{O_2}(+)}{P_T}\right). \qquad (6)$$

The deviation between the lines in the forward and reverse scans was proportional to the scan rate, as shown in Fig. 6. The solid line in the figure shows $\alpha\tau/4FV$ against α when $\tau = 12.9$ s and $V = 5.07 \times 10^{-5}$ mol s^{-1}. This shows that the hystereses of the titration curves in Figs 4 and 5 are reasonably interpreted by considering τ. The amount of reducing gas can be analyzed without knowing τ by using Equation 5. If τ is already given, the amount of reducing gas can also be analyzed by measuring either $P_{O_2}(+)$ or $P_{O_2}(-)$.

4.3. *Comparison of the scan method with the steady-state method*

In our previous paper [2] we showed that the steady-state method, employed to obtain a series of steady-state oxygen partial pressures at given currents, gave reliable analytical values. In the case of the scan method described herein, however, the scan rate influences the shape of the titration curve. On the fast scan the state of the measuring system changes without maintaining a pseudo steady state so that the titration curve has a large hysteresis. On the slow scan the measuring system maintains a pseudo steady state except for the initial time in the forward and reverse scans. Below a scan rate of 3.333 × 10^{-3} mA s^{-1} the titration curve obeyed Equation 4 and long lines, sufficient for precise analysis, were obtained. Comparisons of results by the two methods are shown in Figs 7 and 8. Analytical results are shown in Table 1. Unfortunately, a slight difference in experimental conditions caused an inconsistency between the steady-state and the scan method values. If the same experimental conditions were chosen (except for the method of application of current) the line given by the steady-state method would lie in the centre between the lines by the scan method. The quantities analyzed by the scan method agreed with the nominal values by gas chromatography and were never less reliable than those by the steady-state method.

The steady-state method, based on Equation 1, is an absolute method because Equation 1 is not related to the response behaviour of the measuring system. However, it takes one or two hours to obtain a steady-state titration line. This excessive measuring time results in low analytical accuracy because the mass flow rate of the measuring gas fluctuates due to the changes of atmospheric pressure and room temperature. This disadvantage is overcome by the scan method. As an example, a scan rate of 3.333 × 10^{-3} mA s^{-1} takes only 10 min to scan once. In addition, the quantities of the reducing gas are analyzed on Equation 5 without the need to know the actual response time of the measuring system.

Table 1. Analytical values obtained by the steady-state and scan methods

Method	*% CO × 10^{-2} in Ar–CO*	*% CH_4 × 10^{-3} in Ar–CH_4*
Gas chromatography	2.10	4.76
Steady-state method	2.14	4.70
Scan method scan rate (10^{-3} mA s^{-1})		
0.8333	2.02	4.73
1.6667	1.99	4.71
3.3333	1.98	4.59

References

[1] W. C. Maskell, *J. Phys. E: Sci. Instrum.* **20** (1987) 1156.

[2] H. Taimatsu, H. Kaneko and M. Kawagoe, *Solid State Ionics* **34** (1989) 25.

[3] D. Yuan and F. A. Kröger, *J. Electrochem. Soc.* **116** (1969) 594.

[4] Y. Agrawal, D. W. Short, R. Gruenke and R. A. Rapp, *ibid.* **121** (1974) 354.

[5] H. Taimatsu, H. Kaneko, Y. Uetani and F. Nakatani, *J. Japan Inst. Metals* **46** (1982) 951.

[6] For example see H. S. Carslaw and J. C. Jaeger, 'Conduction of Heat in Solids', 2nd ed., Oxford Univ. Press, London (1959) *passim.*

[7] J. Fouletier, H. Seinera and M. Kleitz, *J. Appl. Electrochem.* **4** (1974) 305.

[8] J. E. Anderson and Y. B. Graves, *J. Electrochem. Soc.* **128** (1981) 294.

[9] *Idem, J. Appl. Electrochem.* **12** (1982) 335.

[10] A. J. A. Winnubst, A. H. A. Scharenborg and A. J. Burggraaf, *ibid.* **15** (1985) 139.

[11] O. Levenspiel, 'Chemical Reaction Engineering', 2nd international ed., Wiley, New York (1972) p. 253.