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Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

CONTRIBUTION TO THE DESIGN AND CONSTRUCTION OF THERMIC FLOW DETECTORS FOR LIQUIDS

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Abstract

Thermic detectors are seldom used in analytical laboratories, in spite of their advantageous properties. Their theoretical basis provides simple relations and useful equations for the design and construction of thermic liquid analyzers. In this paper a home made detector system was used for the continuous determination of hydrochloric acid. The results were in accordance with the theoretical considerations.

Keywords: acid-base determination, liquid thermic detector, process dynamics identification, system theory of flow cell

Introduction

In spite of the fact that thermic analyzers offer versatile possibilities for the determinations of different constituents either in static or dynamic mode, there are only a few applications for the continuous analysis of components of liquid flowing systems. More analytical applications are known for the continuous determination of gaseous components in air, or in gas mixtures [1–3]. The development of liquid detectors needs more extensive experiments and careful selection of proper reagents and reactions for selective and sensitive determinations. Instead of the low reaction rate and low enthalpy change the fast, irreversible ionic reactions with considerable reaction heat are generally preferred.

Theory

Ionic reactions are usually so fast that the temperature change in the flow cell, originating from the enthalpy change of the reaction taking place between the component and the reagent ion, depends only on the geometry of the reactor cell

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and on the mixing conditions. Denoting the analyte ion with A, and the reagent ion with R, and assuming 1:1 reaction, the equation can be as follows:

$$A+R = AR+\Delta H \tag{1}$$

The ionic charges are omitted for simplification. ΔH is the molar enthalpy change of the reaction. If the reaction takes place in an ideally mixed and isolated liquid phase, assuming irreversible reaction, the energy balance will be as follows:

$$-\Delta H c_{\mathrm{AR}} V = (T-T_{\mathrm{o}})\rho C_{\mathrm{p}} \tag{2}$$

According to the conventions, the minus sign before ΔH means exothermic reactions.

c_{AR} is the concentration of the compound formed, V the volume, T_{o} the starting, T the final temperature, ρ the density, C_{p} the heat capacity of the liquid at constant pressure in the cell. Taking also into consideration the heat exchange between the bulk solution and the wall (thermostated to temperature T_{o}) during the residence time, Eq. (2) can be extended as follows:

$$-\Delta H c_{\mathrm{AR}} V = (T-T_{\mathrm{o}})\rho C_{\mathrm{p}} + (T-T_{\mathrm{o}})aA\bar{t} \tag{3}$$

a is the heat transfer coefficient, A the surface area of the wall, $\bar{t}$ the mean residence time. The temperature difference resulted from Eq. (3) is:

$$\Delta T = (T-T_{\mathrm{o}}) = \frac{-\Delta H}{(\rho C_{\mathrm{p}} + aA\bar{t}/V)}\frac{q_{\mathrm{A}}}{q_{\mathrm{out}}}c_{\mathrm{A}} \tag{4}$$

where c_{A} is concentration of the initial (sample) solution, q_{A} and q_{out} are volume flow rates (Fig. 1).

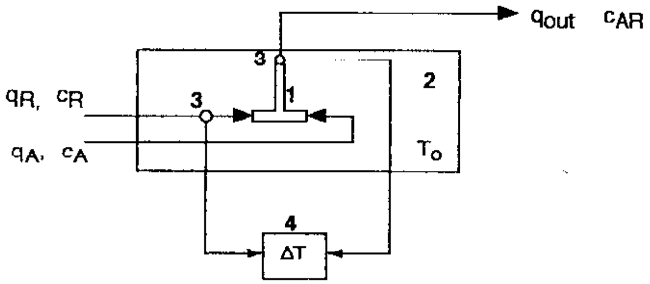

Fig. 1 Scheme of the flow reactor: 1 – reactor cell, 2 – thermostat, 3 – temperature sensors, 4 – measuring instruments. q_{A}, q_{R}, q_{out} flow rate of the analyte, reagent and output, respectively; c_{A}, c_{R}, concentrations

Equation (4) can be used for informatory calculation of the expected temperature difference at given conditions, and given sample concentration.

Example

Determination of hydrochloric acid using sodium hydroxide as reagent.
The data are as follows: $\Delta H = -57100$ J mol^{-1}; $\rho = 10^3$ kg m^{-3} (1 kg l^{-1});
$C_p = 4.18 \cdot 10^3$ J kg^{-1} °C^{-1}; $a = 1.16 \cdot 10^3$ J m^{-2} °C^{-1} s^{-1} (20°C);
$A = 200 \cdot 10^{-6}$ m^2 ; residence time in the cell: $\bar{t} \sim 1$ s ;
$V = 200 \cdot 10^{-9}$ m^3 (200 μl); $c_A = c_{HCl} = 20$ mol m^{-3} (0.02 mol l^{-1});
$c_R = c_{NaOH} = 100$ mol m^{-3} (0.1 mol l^{-1}); $q_{HCl} = q_{NaOH} = 100 \cdot 10^{-9}$ m^3 s^{-1}.
The expected temperature difference using Eq. (4):
$\Delta T = [57 \cdot 10^3/(10^3 \, 4.18 \cdot 10^3 + 1.16 \cdot 10^3 \cdot 200.1/\,200 \cdot 10^{-3})]0.5 \cdot 20 = 0.106$°C

The calculations above, however, do not yield any information concerning the time-dependence of the measurable temperature signal difference. Since the signal response evolves in time, the characteristic dynamic properties of the detector system must be known. Although delay times may be predicted from the geometry of the tubes and the cell, and from the estimated time constants of the flow rates, the best and most reliable identification of a dynamic system is direct measurements under fixed, but different conditions. In this studies it is assumed that the system is a linear and has no time dependence, therefore the relation between the input and output signals can be described by a well-defined differential equation. In the case of the detector flow cell it must be considered that there are at least two independent time constants, originating from the residence time and from the hydrodynamic properties of the mixing process, and there is usually a delay time originating from the time difference between the sample introduction and the starting point of the mixing. Thus, the differential equation is of second order with a delay time constant. For the determination of the time constants and the delay time value, measurements have to be carried out with the analyzer itself, using known concentration profiles in the sample solutions and registering the measured output signal (temperature difference) continuously, or with close periodicity in time. Assuming a process of second order, the two time constants (τ_1 and τ_2) and delay time (τ_d) can be determined by curve fitting from the registered signal value series, using the following step response function:

$$y(t) = y_o + y_{\mathrm{step}}\left[1 + \frac{\tau_1}{\tau_2 - \tau_1} e^{-(t-t_d)/\tau_1} - \frac{\tau_2}{\tau_2 - \tau_1} e^{-(t-t_d)/\tau_2}\right] \tag{5}$$

In the case, when $\tau_1 = \tau_2 = \tau$, the equation is simplified to:

$$y(t) = y_o + y_{\mathrm{step}}\left[1 \quad \left(1 + \frac{t - t_d}{\tau}\right) e^{-(t-t_d)/\tau}\right] \tag{6}$$

Thus, by the curve fitting process, the time constant(τ), the delay time and the signal maximum value (y_{step}) can be estimated from the obtained series of signal values. y_0 is usually zero.

Note
The Eqs (5) and (6) correspond to the following Fourier transfer functions with time shift, respectively [4]:

$$H_2(\omega) = \frac{1}{(1+i\omega\tau_1)(1+i\omega\tau_2)} \quad \text{and} \quad H_1(\omega) = \frac{1}{(1+i\omega\tau)^2}$$

y_{step} the maximum value of the registered response signal curve corresponding to the step height of the input concentration function, $c_{A,step}(t)$. The ratio of the two values is called the sensitivity of analysis.

Experimental

A detector system was constructed as shown in Fig. 2. A reactor tube of variable length was immersed in a thermostat kept at 20°C, and a selector valve was installed in the entering stream. While the reagent sodium hydroxide solution of constant concentration was flowing continuously, in the other channel the flow of water was changed suddenly using the selector valve for the introduction of sample solution containing hydrochloric acid of known concentration. The turning of the valve, i.e. the introduction of the sample, was commanded by a microprocessor attached to the computer, and in the same time the measurements between the two temperature sensors (thermistors) started, and the values were recorded in digital form. The solutions were fed with a peristaltic pump.

An analog circle was constructed and used for measuring the difference of the thermistors (corresponding to the temperature difference, T–T_0). The signal difference was amplified, filtered using a low pass filter, digitized and stored for il-

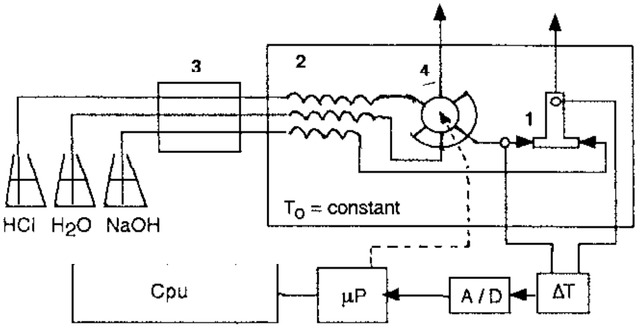

Fig. 2 Thermic detector system for the determination of hydrochloric acid in solutions:
1 – flow detector cell, 2 – thermostat, 3 – peristaltic pump, 4 – six-way valve for sample introduction

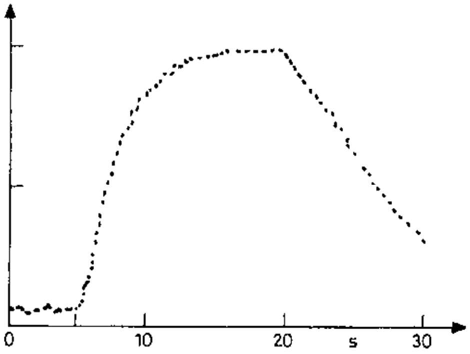

Fig. 3 Response signal value diagram, obtained by the thermic detector system, on the effect of the sample solution of 0.02 mol l^{-1} concentration introduced stepwise

lustration and calculations. For details see [6]. A diagram of the measured signal values as a function of time can be seen in Fig. 3. The measurements were carried out with different flow rates, with different reactor cell lengths and with different concentrations of the sample solution. Using the signal values of the first (ascending) parts of the diagrams obtained, the delay time, time constant and the linear transfer factor (signal maximum) the base line values were calculated using the curve fitting method based on the Gauss-Newton principle.

It was found that the time constants and the signal maxima were very similar, irrespective of the volume of the cell (88 or 339 μl). The dispersion of the signal was caused primarily by the inlet tubes rather than by the mixing cell. Therefore the smaller cell volume was selected. By increasing the flow rates in the range of 50 –500 μl s^{-1} the time constants decreased remarkably. At high flow rates, however, the signal to noise ratio became significant. Thereafter the flow rate of 210 μl s^{-1} was used.

The results of the measurements and calculations were as follows:
The time constants were found to be very close to each other. The mean value, calculated from 30 measurements, using various concentration step values was:

$\tau=\tau_1=\tau_2=1.5$ s (standard deviation: 0.14). The delay time, $t_d=5.0$ s.

Good linear correlation was found between the obtained signal maximum values and the concentrations of the sample solutions, in the range of $0.5\cdot10^{-2}$–$3\cdot10^{-2}$ mol l^{-1}. The relative standard deviation was less than 3% [6].

Conclusions

Equation (3) is applicable for the calculation of the expected temperature difference caused by the heat of reaction which takes place between the analyte and a reagent under ideal conditions, i.e. when the reaction is fast compared to the mixing rate. If the reaction rate is not sufficient in room temperature, a higher temperature, T_0 may be selected, but it should be kept in mind that by increasing the temperature the noise is also increasing, which is not desirable. Equation (3) is also very useful for the estimation of the possible interferences which may present in the sample solution. The extent of the interferences can be estimated by calculations, if the approximate concentrations of the components and the corresponding heat values of the reactions are known.

> *Note*
> If the reaction rate is low, the kinetics of the reaction can be investigated, and the kinetic parameters determined, from the temperature values measured during the reaction, using a well mixed batch reactor (calorimeter) system [7].

For the study of the time history of the produced signal in a flow reactor system, the best approach is to carry out measurements with the instrument and to investigate the obtained step reaction signal functions. The results of the analysis of the step reaction functions, using Eqs (5) or (6) give very precious information to the optimization of the flow rate, detector cell form and size, and to the proper construction of the connecting tubing.

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