Analytical Methods

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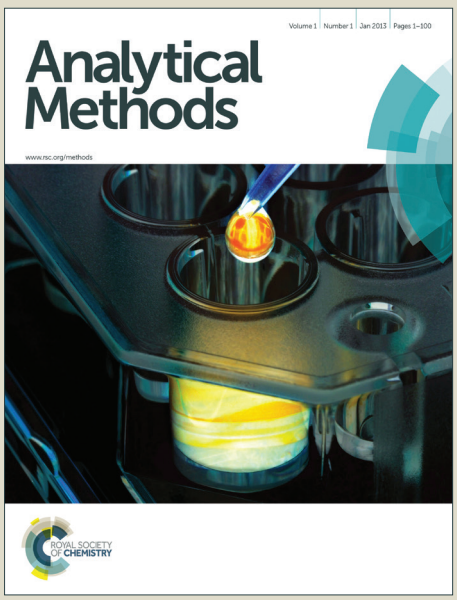

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Simultaneous determination of Peracetic acid and Acetic acid by titration with NaOH

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This article describes and evaluates a titration for simultaneous determination of peracetic acid (PAA) and acetic acid (HAc) in an aqueous solution.

The titration is a classic acid-base titration based on the significantly different pKa of PAA and HAc. In contrast to most of the methods used to assay PAA in aqueous solutions, this method is well suited for automatic determinations.

The validation shows that this method is simple, precise, has a high repeatability and is robust to a number of errors known from other PAA determination methods.

Introduction:

Peracetic acid is widely used as a disinfectant, and is commonly produced "in situ" by mixing Acetic acid and Hydrogen peroxide (H_2O_2) in an aqueous solution. The equilibrium (Eq. 1) has an equilibrium constant somewhere between 2 and 3[1-3] which means that there will always be significant concentrations of all the species when equilibrium (Eq.1) is reached.

$$CH_3COOH+H_2O_2 \leftrightarrow CH_3COOOH+ H_2O \qquad (Eq.1)$$

The reaction only reaches its equilibrium after a considerable time and is furthermore influenced by other factors like temperature or pH of the solution etc. Therefore, it is vital to have fast and precise methods to analyze PAA-products and solutions, to ensure they match the desired specifications.

The traditional, and still widely used, methods to determine PAA is redox titrations where PAA oxidizes iodine to iodide which is then titrated with thiosulfate. A problem with this is that hydrogen peroxide is also an oxidant that oxidizes iodine. One way around this was to titrate H_2O_2 with permanganate[4] before the iodometric titration was performed. The analysis was later improved by replacing permanganate with Cerium(IV)[5].

These double titrations have however some drawbacks, as the original authors[4,5] already were aware of and others since have studied in details[6]. As mentioned manganese ions can participate in redox reactions, and on the other hand the cetrimetric titration requires an indicator (e.g. Ferroin) which also participates in the redox equilibrium and furthermore masks the iodometric color change. And finally there is an inherent problem with both methods in the fact that the titration requires sulfuric acid, which will catalyze any shift the PAA-equilibrium.

Other methods have been developed e.g. a single iodometric titration taking advantage of the different reaction speeds of the iodine-oxidation of H_2O_2 and PAA respectively[7], or methods based on other principles than titration, for example spectrophotometric[8,9,10], electrophoretic[11] or by HPLC[12] . A drawback of the latter methods is that they generally require more advanced equipment and has to be calibrated with reference to one of the titration methods, in the absence of certified PAA standards.

The analytical method described in this paper is an acid/base titration relying on the fact that PAA is a much weaker acid than acetic acid. A potentiometric titration can therefore easily separate the equivalence points of these two acids in a solution.

The principle was first described in a patent application[13] but has, to the best of the author's knowledge, not been described in any detail in the scientific literature. This work therefore investigates aspects of the titration, such as precision, linearity and robustness.

Materials and methods:

It is not possible to obtain a certified sample of peroxyacetic acid, on which the methods accuracy could be determined, since the equilibrium is highly sensitive to influences of e.g. temperature, and furthermore both PAA and H_2O_2 are reactive species susceptible to decay even in stabilized solutions.

The batch used in this work was made in the laboratory from a mixture of 49.89% (w/w) H_2O_2 and 99.6% Acetic acid. The concentration of H_2O_2 in the reagent was determined by measuring density (PAAR Density meter) using tabulated values. The acetic acid was titrated with NaOH (0.5M) using phenolphtalein as an indicator.

The batch developed at 40°C for around one week while the content of PAA was monitored, and when equilibrium seemed to be reached, the rest of the analyses were made over a number of days.

The Acetic acid/PAA titrations were performed on a Mettler DL25 automatic titrator, equipped with a Mettler pH-electrode, using 0.5 M NaOH as titrant. The titrant was standardized against an oxalate standard regularly. All reagents were analytical standard (VWR).

For a typical titration, a sample of the test solution was precisely weighed (±0.001g) into a beaker and diluted to 40ml with demineralized water. The beaker was placed on the titrator and the analysis was performed swiftly. The whole procedure, from

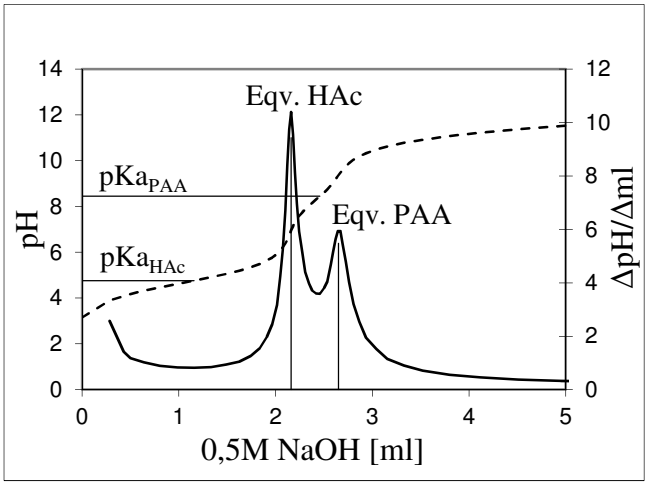
weighing the sample till both acids were determined, took usually less than 5 min, minimizing any effect of change in temperature, dilution etc.
Series of tests were performed to evaluate linearity and the effect of dilution, by weighing different amounts of sample. The linearity was tested by a regression analysis using Excels Data Analysis Tool, and R^2 was used as indicator of linearity.
Quantification (QL) limit was calculated using the formula (Eq. 2):

$$QL[\text{g Sample}] = \frac{10 \cdot \sigma\ [\text{mmol}]}{S\ \left[\frac{\text{mmol}}{\text{g Sample}}\right]} \quad \text{(Eq. 2)}$$

Where σ is the standard deviation of 6 samples weighing 0.10g±0.01g, and S is the response. In this paper the slopes from linearity determination are used as response. QL was calculated for both PAA and acetic acid.
To test the robustness of the analysis samples were spiked with different amounts of Acetic acid, Hydrogen peroxide and Sulfuric acid.
A bias in the original method from D'Ans & Frey[3] was that prolonged analysis time caused a lower PAA result. This effect was not significant in the Ce-titration[5] but is an inherent problem that should be addressed. The equilibrium (Eq. 1) shows that increased water concentration will shift the balance back towards lower PAA, an effect catalyzed by the sulfuric acid necessary for both the MnO_4 and Ce titrations. To address this effect a series of dilutions were analyzed at different time intervals after weighing and dilution.

Results:

Fig. 1 Example of titration curve (dotted line) and derivative curve (full line).



In Fig. 1 at typical titration curve is presented, superimposed by the derivative curve (ΔpH/Δml) which emphasizes the equivalence points. In the figure pKa of both acids can also be read as the pH at which the buffer capacity is highest (= lowest ΔpH/Δml).

Table 1: pKa of the two acids

	Published values	From titration
Acetic acid	4.75	4.72
Peracetic acid	8.2 [9]	8.3

The pKa's from Fig. 1 is listed in Tab. 1 and compared with publicized values.

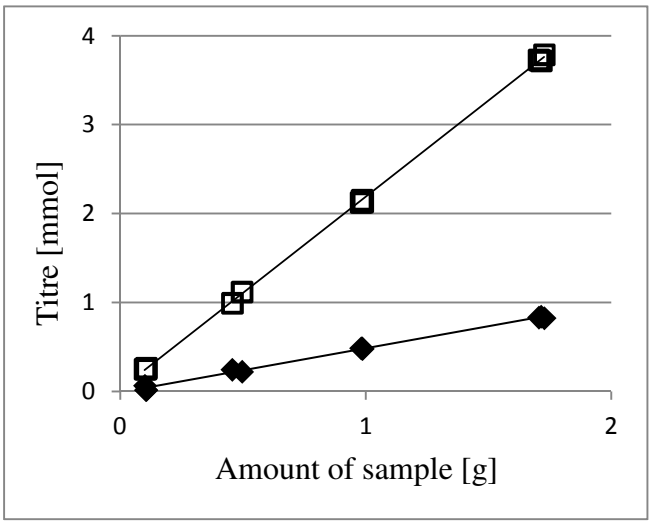


Fig. 2 Linearity for HAc (□) and PAA (◆). Lines are from regression, $R^2 > 0.99$ for both

Figure 2 shows the linearity of titration samples of different sizes. The result is presented as titer of acids as a function of sample size. The figure shows both the linearity of the titration itself and the effect of diluting the sample, since the different amounts of sample in all cases were diluted to 40ml. The slope of the lines respectively equals the average amount of PAA (=0.498 mmol/g) and Acetic acid (=2.181 mmol/g) in the batch.
Compared to the original amount of Acetic acid used in the batch, the sum of the titrated species gives a recovery of 100.6%.

Table 2: Amount of acids in samples (mean±std.dev.) and QL for PAA and HAc

Sample [g]	Titrated acids [mmol]	QL [g sample]
0.09 ±0.01 (N=6)	HAc: 0.23±0.03 PAA: 0.040±0.005	HAc: 0.13 g PAA: 0.09 g

Table 2 shows results from 6 determinations of small samples (around 0.1 g). The Quantification Limits are calculated according to Eq. 2, using standard deviation (σ) from the 6 results for each acid individually and the slopes (S) taken from the regression lines in Fig. 2.
From the data in Tab. 2 the relative coefficient of variation (CV%) can be calculated to 13% for both acids. A similar estimate can be made based on the statistics from the regression (Fig. 2) resulting in 0.5% for PAA and 1.5% for HAc (data not shown in detail).
Table 3 shows results from analyzing samples spiked with different combinations and amounts of acetic acid and hydrogen peroxide, and a sample without spike for comparison. The solutions used for spiking were the same chemicals used to make the samples originally.

Table 3 Samples spiked with HAc and/or H_2O2. Results are mean ± standard deviation.

Sample [g]	Spike		Recovery HAc [%]	Recovery PAA [%]
	HAc [g]	H_2O_2 [g]		
0.53 ±0.04 (N=2)	0.995±0.003	0	98.9±0.2	102.94±0.03
0.53±0.01 (N=2)	0	1.014±0.001	100.1±0.5	97±1
0.51 (N=1)	1.011	1.002	98.6	100.3
0.53 ±0.04 (N=2)	0.995±0.003	0	98.9±0.2	102.94±0.03

Recovery of PAA is calculated relative to the content found in samples without spike and recovery of HAc relative to the sum of the unspiked samples and added acid.
Sulfuric acid spike solution was a 4.8% H_2SO_4 made from 96% H_2SO_4 (commercial grade). The exact concentration in the spike solution was determined by titration and used for calculating sulfuric acid recovery, as listed in Tab. 4.
Recovery of PAA and HAc is calculated relative to the amount found in the unspiked sample.

Table 4 Results from spiking samples with different amount of sulfuric acid. Results are mean ± standard deviation.

Sample [g]	Spike H_2SO_4 [g]	H_2SO_4 [%]	Recovery PAA [%]	HAc [%]
0.48±0.02 (N=2)	1.008±0.003	99.7±0.7	99±2	99.1±0.2
0.56±0.03 (N=2)	2.04±0.01	98.9±0.1	97.727±0.003	100.26±0.01
0.53±0.03 (N=2)	4.125±0.009	99.05±0.01	95.2±0.5	100.5±0.3

Figure 3 shows the effect from increasing time delays from dilution to analysis. Five samples at app. 1 g were simultaneously diluted to 40ml with demineralised water. One was titrated immediately (Time=0) and the rest were left at ambient temperature for app. 15, 30 and 60 minutes, and then titrated.

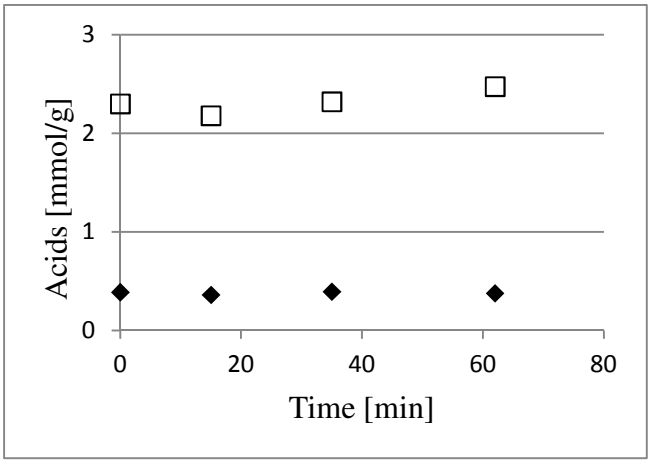


Fig. 3 Concentrations of HAc (□) and PAA (◆) analyzed at different intervals from dilution to titration.

There is no significant change in the concentration of either acids as a result of the delay.

Conclusions

The titration curves (Fig. 1) clearly shows that the titration is capable of detecting and separating peracetic acid from acetic acid.
The linearity of the dilutions seen in Fig. 2, together with the acetic acid and hydrogenperoxide spiking (Tab. 2), demonstrates the feasibility of the method, when applied to samples of varied composition. The recovery of the spiked samples are generally very close to 100%, showing that variable amounts of acetic acid or hydrogen peroxide does not affect the result
Truly, the data in Fig. 2 and the calculated QL only shows range and linearity for a product of this particular compsition. There is, however, no reason to expect fundamental differences when analyzing other ratios of HAc/PAA/H_2O_2, especially considering the high recovery from the spiked samples. QL and range of linearity will off course largely depend on details in method and type of equipment.
Vidan & de Lago[11] obtained CV% of approximately 4% for both PAA and HAc using capillary electrophoresis. In the same paper they report a CV% of 0.3% when titrating PAA with the method of Greenspan & MacKellar[5] (titration with Ce). From the data of Sully & Williams[7], CV% in the range of 1.7% - 0.3%, for both cetrimetric and iodometric titrations, can be calculated. In comparison, the results obtained in this work, with a CV% of 13% close to QL and significantly lower over the the rest of the measuring range (down to 0.5-1.5%), demonstrates that this method has a repeatability comparable to other analytical methods.
Delay after dilution has no influence on the result. Time delay effects has previously been noted when using other titration methods[5] and is generally explained by competitive reations in the solution during the proces of titration.
When spiking with sulfuric acid, increased amount seems to decrease the PAA content slightly while acetic acid increases. The changes are minute but notable, and can be explained by the catalytic effect of sulfuric acid which will enchance the effect of dilution and shift the equilibrium towards lower PAA concentration.
It is well known that peracetic acid hydrolyses faster when pH is high. This could cause this method to give too low PAA results. Yuan et al.[14] determined the decomposition of PAA at different alkaline pH and temperatures. Using their model it can be estimated that even if the highest decomposition rate was assumed at most 2% of the initial PAA is lost through decomposition, over a period of 10 minutes (at 20°C) which is more than adequate to complete a titration. And only a part of the titration actually takes place at such high pH. The overall good recovery of acids seen in this work, also support the assumption that the loss to decomposition is negligible.
One drawback with this method is the interferrence of other weak acids. An example would be 1-Hydroxyethane 1,1-Diphosphonic acid (HEDPA) which is an often used stabilisator in peracetic and hydrogenproxide solutions. It is a tetra-protic acid with pKa = 1.7, 2.5, 7.3 and 10.3 and at least the two medium acid protons will be hard to distinguish from HAc and PAA respectively. HEDPA is normally applied in concentrations up to 1%. At this concentration it will bias the calculations by increasing HAc 0.3% and PAA

0.4%. In contrast, the traditional redox titrations have some practical issues that the titration described here avoids: It does not need to be performed at low temperature and it does not need significant amounts of sulfuric acid, and furtermore this method is well suited for automatisation.

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This paper describes a fast and easy method to analyze peracetic acid in mixtures with both acetic acid and hydrogenperoxide.