

On the Use of the Senses of Taste and Smell in Determining the End Point of an Acid-Base Titration

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While the sense of taste is hardly applicable to the fixation of the end point of a titration, the examination reported in the following shows that the sense of smell is quite applicable. Five different smell indicators are mentioned: Sodium butyrate, sodium sulphide, quinoline, pyridine, and ammonium chloride, the first four of which are applicable in the strong acid/strong base titration with an uncertainty on the single determination of 0.2 % or less.

The recognition of the end point of a titration is based either on a visual impression or on a measurement of a physical quantity which is altered at or in the neighbourhood of the equivalence point. In the former case use is made of the sense of sight, but the question forces itself on one as to whether other senses could be used. In ancient chemistry the senses of taste and smell were used as much as possible; in the 18th century it was customary to use the taste of a substance — among other criteria — as a qualitative test, and also the smell of the substance was observed whenever possible.

Also when neutralizing with preparative purposes the sense of taste was used. By way of example may be quoted de Lassone¹, who wished to prepare ammonium acetate: "Lorsque par le mélange successif de l'esprit acéteux et de l'alkali volatile, on est parvenu à une saturation exacte et complète, ce que la saveur et les autres indices font reconnoître."

However, the estimation of the sense of taste as a chemical help decreased, and the use of it became extinct. Thus already Bergmann (quoted from Tabor's German translation of Bergmann's Latin text)² wrote as follows in "Meditationen über das System der Fossilien":

"*Geschmack*. Dieser hängt von der Empfindlichkeit der Zunge ab, und ist, wie die Erfahrung lehret, sehr verschieden, denn was bey dem einen die Nerven=Wärzgen merklich reizet, reizet sie bey einem andern nicht. Man kann also auf diese Eigenschaft nur sehr wenig bauen."

In 1898, however, Richards³ made the question of the possible applicability of the sense of taste in titrations the subject of a debate. He found

that the taste of a 0.001 N strong acid can be recognized, and that it should therefore be possible to fix the end point of a strong acid/strong base titration with an accuracy of 1—2 %. He reported a few experiments with still better results (greatest deviation 0.9 %).

We have tested the strong acid/strong base titration (25 ml 0.1 M hydrochloric acid with 0.1 M sodium hydroxide and *vice versa*) and found that it is not possible with any certainty to taste the difference between solutions with pH between just under 3 and just under 11 (*i. e.* that OH^- can be tasted in a little lower concentration than H_3O^+). We did find that the end point in such a titration cannot be fixed by means of the sense of taste with deviation of less than 2 or 3 %. Even though individual differences are attached to the sense of taste, it can be established that the taste cannot with any reasonable accuracy be used in this way as indication in the strong acid/strong base titration.

As, for various reasons, any method based upon the taste must be inadequate, we have not wished to continue working in this direction. We may add only that the sole possibility of obtaining results of any reasonable accuracy by means of the sense of taste will probably be to add a taste indicator, *i. e.* a weak acid-base system, in which the weak acid has a different taste from that of the corresponding weak base.

As to the use of the sense of smell in titrations an article on this subject was written in 1913 by Sacher⁴. He titrated *isovaleric* acid with an excess of sodium hydroxide and titrated back with hydrochloric acid, since the appearance of the smell of *isovaleric* acid is more easily recognizable than the disappearance. He further titrated ammonia with hydrochloric acid until the disappearance of the smell of ammonia. He also tried to titrate acetic acid and phenol. In all cases he obtained results that group themselves around the theoretical results, but with rather great deviations (up to 6 %).

We are of the opinion, however, that if the sense of smell has to be used in connection with a titration, it must be done by adding to the titration system a smell indicator, which in an acid-base titration should be a weak acid-base system in which the weak acid has a different smell from that of the corresponding weak base.

As indicators of this type the following substances have been examined: 1) Sodium butyrate, 2) sodium sulphide, 3) quinoline, 4) pyridine, and 5) ammonium chloride. Of all five indicators a weak acid-base system can be made, one component of which is odourless, and the other has a characteristic smell. In all experiments mentioned in the following, titrations were carried out until the appearance of a smell.

0.1 M sodium hydroxide, free from carbon dioxide, was used in the experiments, and the solution was standardized against hydrazine sulphate. Further 0.1 M hydrochloric acid was used (the same hydrochloric acid in the experiments in connection with the first two indicators and a different hydrochloric acid in connection with the last three indicators). *Ca.* 25 ml titrand was used and to this was added 21—22 ml titrator. It was not till then that the indicator was added, and titration was made by dropwise addition of titrator.

1) *Indicator 0.01 M sodium butyrate* ($\text{p}K_s = 4.8$ for butyric acid). Titrand NaOH; titrator HCl. The molarity of the hydrochloric acid was found to be

Table 1. Determination of the molarity of a hydrochloric acid by means of titration of standard sodium hydroxide and with a 0.01 M sodium butyrate as smell indicator.

Expt. series	Number of expts.	Quantity of indicator ml	Molarity of HCl (found)	Greatest deviation from mean value	Uncertainty in % on single determination	Uncertainty in % on mean value
I	10	0.10	0.1002	0.0005	0.3	0.10
II	10	0.10	0.1001	0.0005	0.4	0.13
III	10	0.05	0.1002	0.0005	(0.3)	(0.11)
IV	10	0.10	0.10020	0.0003	0.2	0.07

0.10046, if methyl red was used as indicator. (Mean value of 10 determinations; greatest deviation from mean value 0.00010; uncertainty on a single determination 0.07 %; uncertainty on the mean value 0.02 %.)

The results are given in Table 1. In series I a smelling liquid was used for comparison, whereas the other series of experiments were performed without such a liquid. In series III, three of the experiments were unsuccessful owing to the small quantity of indicator; the calculations of uncertainty were carried out for the remaining 7 experiments. Series IV was carried through exactly as No. II, and it is seen that training in the recognition of the smell of butyric acid may increase the accuracy.

Besides, the butyric acid was found to be easily liberated by local excess of a strong acid, which fact may lead to a wrong estimation of the end point; the hydrochloric acid should therefore be added carefully and the addition be accompanied by vigorous shaking.

Conclusion: After some training in the use of the method, 0.10 ml 0.01 M sodium butyrate can be used as a smell indicator in the titration of strong acid/strong base; uncertainty on a single determination *ca.* 0.2 %.

2) Indicator 0.01 M sodium sulphide ($pK_s = 7.2$ for hydrogen sulphide). Titrand NaOH; titrator HCl. The molarity of the hydrochloric acid was found to be 0.10068 when bromothymol blue (6.0—7.6 in pH) was used as the indicator. (Mean value of 10 determinations; greatest deviation from mean value 0.00011; uncertainty on a single determination 0.06 %; uncertainty on the mean value 0.02 %.)

The results are given in Table 2. In series I and III, but not in series II and IV, a smelling liquid was used for comparison. It is seen that this comparison liquid is unnecessary. Liberation of hydrogen sulphide in connection

Table 2. Determination of the molarity of a hydrochloric acid by means of titration of standard sodium hydroxide and with a 0.01 M sodium sulphide as smell indicator.

Expt. series	Number of expts.	Quantity of indicator ml	Molarity of HCl (found)	Greatest deviation from mean value	Uncertainty in % on single determination	Uncertainty in % on mean value
I	6	0.10	0.10068	0.00023	0.15	0.06
II	6	0.10	0.10074	0.00025	0.15	0.06
III	6	0.05	0.10079	0.00018	0.15	0.06
IV	6	0.05	0.10077	0.00019	0.14	0.06

Table 3. Determination of the molarity of a hydrochloric acid by means of titration with standard sodium hydroxide and with a 0.01 M quinoline as smell indicator.

Expt. series	Number of expts.	Quantity of indicator ml	Molarity of HCl (found)	Greatest deviation from mean value	Uncertainty in % on single determination	Uncertainty in % on mean value
I	6	0.10	0.1002	0.0004	0.29	0.12
II	6	0.10	0.1002	0.0002	0.19	0.08
III	6	0.20	0.10023	0.00030	0.20	0.08
IV	6	0.20	0.10029	0.00018	0.14	0.06

with local excess of acid during the titration did not take place to any disturbing degree — in contradistinction to what was the case with butyric acid.

Conclusion: Without special training sodium sulphide can be used as a smell indicator in the titration of a strong acid/strong base; uncertainty on a single determination *ca.* 0.15 %.

3) Indicator 0.01 M quinoline dissolved in 20 % ethanol ($pK_a = 4.9$ for quinolinium ion). Titrand HCl; titrator NaOH. The results are given in Table 3. A smelling liquid was used for comparison in series I and III, but not in

Table 4. Determination of the molarity of a hydrochloric acid by means of titration with standard sodium hydroxide and with a 0.01 M pyridine as smell indicator.

Expt. series	Number of expts.	Quantity of indicator ml	Molarity of HCl (found)	Greatest deviation from mean value	Uncertainty in % on single determination	Uncertainty in % on mean value
I	6	0.10	0.10019	0.00019	0.14	0.06
II	6	0.10	0.10039	0.00028	0.14	0.06
III	6	0.20	0.10021	0.00025	0.13	0.05
IV	6	0.20	0.10029	0.00023	0.15	0.06

series II and IV; it is seen that this liquid is unnecessary. Liberation of quinoline in local excess of base during the titration did not take place to any disturbing degree. About one half of the experiments with addition of only 0.05 ml 0.01 M quinoline were unsuccessful.

In the titrated solutions pH (electrometrically found) was 6.1 on an average; the deviations from the mean value of pH corresponded well to the deviations of the results from the mean value of these.

Conclusions: Quinoline is quite applicable as a smell indicator in the titration of strong acid/strong base; uncertainty on a single determination *ca.* 0.2 %.

4) Indicator 0.01 M pyridine dissolved in water ($pK_a = 5.2$ for pyridinium ion). Titrand HCl; titrator NaOH. The results are given in Table 4. In series I and III a comparison smelling liquid was used; it is seen that this liquid is superfluous. The sense of smell appears to be somewhat dulled by pyridine if the experiments are carried out one immediately after the other. In the experiments reported here the titrations were performed with intervals of about 7 minutes. Eight out of ten experiments with addition of only 0.05 ml 0.01 M pyridine were unsuccessful. In the titrated solutions pH was 6.9 on an average.

Table 5. Determination of the molarity of a hydrochloric acid by means of titration with standard sodium hydroxide and with a 0.01 M ammonium chloride as smell indicator.

Expt. series	Number of expts.	Quantity of indicator ml	Molarity of HCl (found)	Greatest deviation from mean value	Uncertainty in % on single determination	on mean value
I	6	0.20	0.1007	0.0001	0.10	0.04
II	6	0.20	0.1012	0.0006	0.49	0.20

Conclusion: Pyridine is quite applicable as a smell indicator in the titration of strong acid/strong base; uncertainty on a single determination *ca.* 0.15 %.

5) Indicator 0.01 M ammonium chloride ($pK_s = 9.3$ for ammonium ion). Titrand HCl; titrator NaOH. The results of the experiments are shown in Table 5. In series I a comparison smelling liquid was used, which was not the case in series II. The comparison liquid is useful here, but the sense of smell should be accustomed beforehand to the smell of ammonia. A smaller quantity than 0.20 ml 0.01 M NH_4Cl could not be used; with 0.10 ml most of the experiments were unsuccessful. In the titrated solutions pH was 10.0 on an average.

Conclusion: Ammonium chloride can be used as a smell indicator, even though its applicability does not come up to that of the indicators mentioned above.

Consequently, it is possible to carry out acid-base titrations using smell indicators. In the titration of weak acids or bases an indicator system with a suitable pK_s should be used. The titrations can be carried out in coloured solutions and require here no special apparatus (as *e. g.* ultraviolet radiation when using fluorescence indicators, conductance cells, *etc.*).

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