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Short communication

Quantitative thin-layer chromatography of perbromate

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Abstract

A thin-layer densitometric micromethod for the determination of perbromate is described using Merck 5577 microcrystalline cellulose thin layers with butanol–10% ammonia as solvent. The spots are evaluated by a starch–iodide reagent in 6 *M* HCl using the Cybertech Gel documentation system WINCAM 2.1. The method was used to determine perbromate in an aged dilute solution and in an impure solid sample.

1. Introduction

The perbromate ion was discovered by Appelman in 1968 [1] and although over hundred papers have been written on its properties, only several kilogrammes of it have been synthesized so far. When trying simple methods of synthesis we noted that besides the paper and thin-layer chromatographic separation described by Lederer and Sinibaldi [2] there was no simple test for the presence of perbromate in solution.

Most analytical reactions are based on the liberation of iodine during the reduction of perbromate in the presence of iodide. This can be made more selective by first reducing the bromate; however this reaction seemed to be too unspecific unless preceded by a separation. Besides the reduction reaction, perbromate, like perchlorate, yields a red spot on paper when reacted with methylene blue [2]. While this test would readily distinguish it from bromate and bromide, it is not readily quantitated, because a red spot on a blue background does not give a good contrast in a colorimetric determination.

As shown by Lazarou et al. [3] as well as others, perbromate does not react instantaneously with KI. Thus a scanning technique in which the chromatogram is passed under a photoelectric device would not be satisfactory. A chromatogram sprayed with iodide would liberate further iodide due to its access to air as well as evaporate iodine in addition to a slow formation of the actual colour to be determined.

Recently a CCD camera arrangement was constructed by Cybertech (Berlin) principally for the determination of the intensity of bands obtained by electrophoresis in nucleic acid sequencing. The instrument produces a photographic image of the entire electropherogram or chromatogram, so that in the case of the perbromate reaction with iodide one can obtain a series of standards together with the sample to be analysed exactly at the same moment. Furthermore the data thus obtained can be treated by a computer and directly give the calibration curve and the spot intensities of the sample spots on the same thin layer.

Below we describe the application of this arrangement for the determination of perbromate and the application of the method to the

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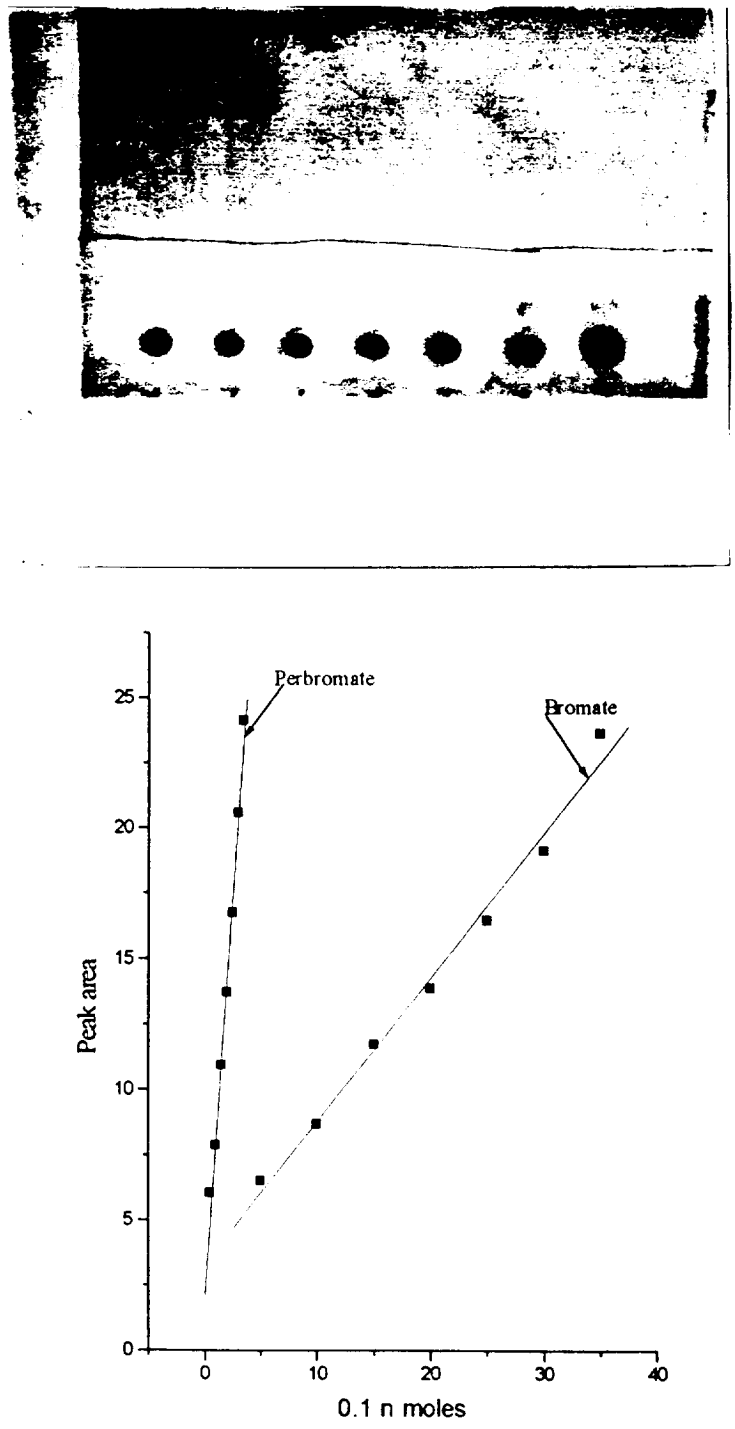
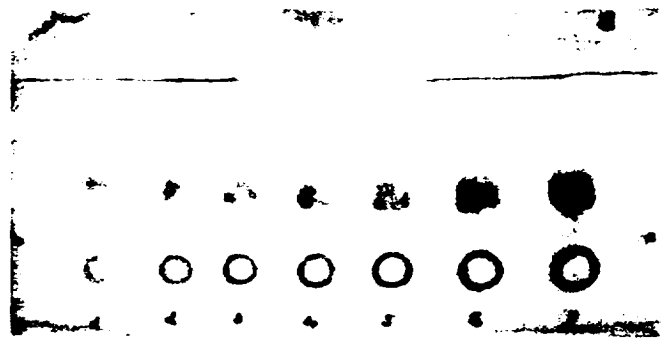


Fig. 1. Calibration curve of mixtures of perbromate and bromate in ratio 1:10. Top: The photo obtained by the CCD camera. Below: The calibration obtained from the densitometric results. Perbromate: $y = (6.10 \pm 0.25)x + 2.09 \pm 0.55$; $r = 0.9960$. Bromate: $y = (0.55 \pm 0.03)x + 3.29 \pm 0.58$; $r = 0.9945$.



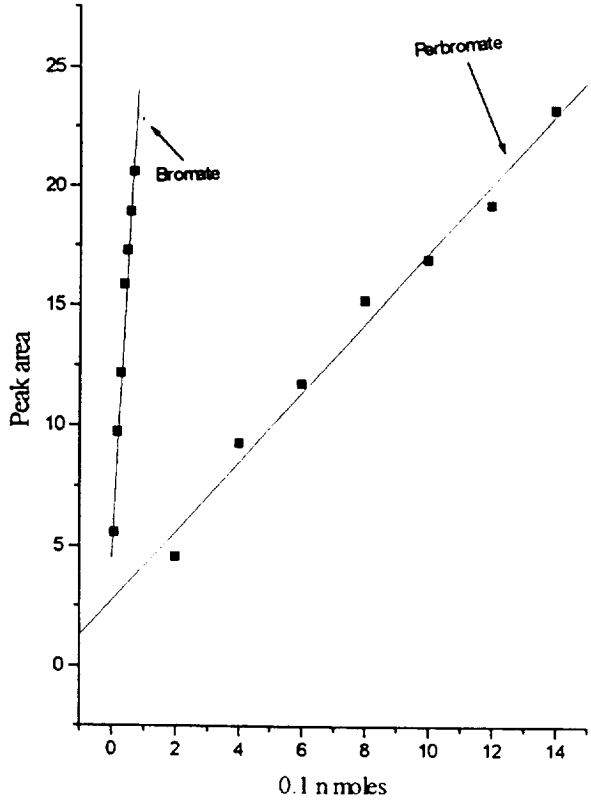
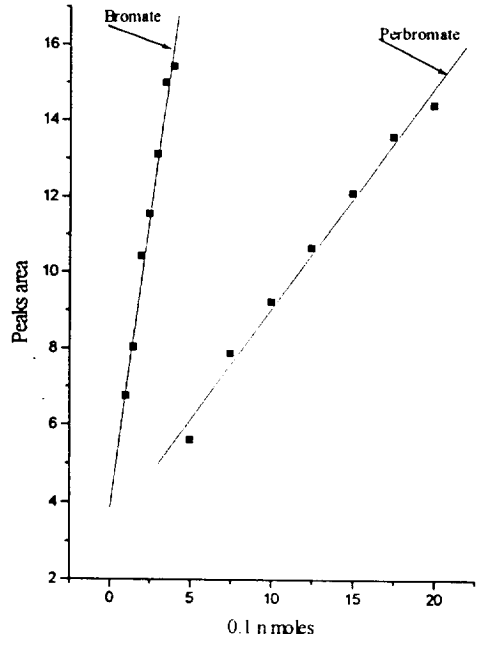
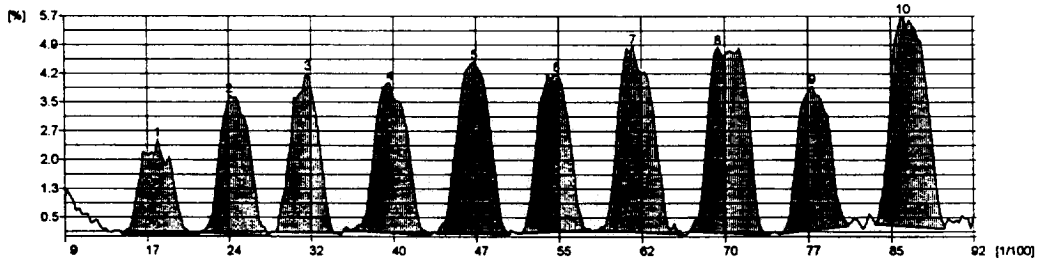


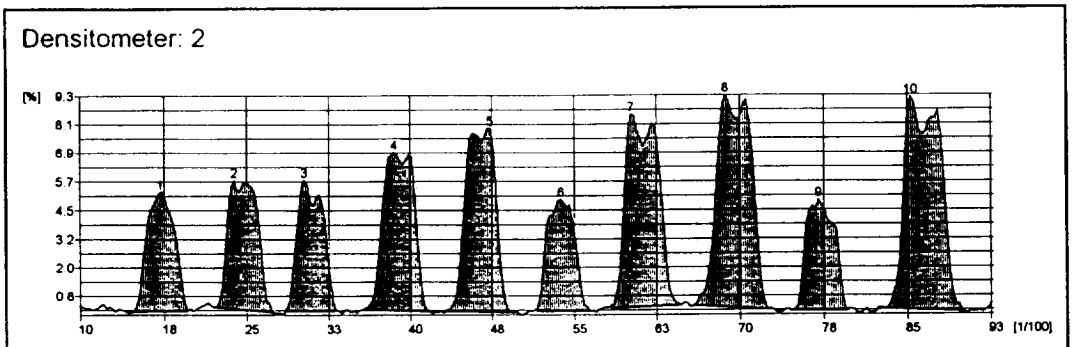
Fig. 2. Calibration curve of mixtures of perbromate and bromate in ratio 20:1. Top: The photo obtained by the CCD camera. Below: The calibration obtained from the densitometric results. Perbromate: $y = (1.44 \pm 0.08)x + 2.72 \pm 0.72$; $r = 0.9924$. Bromate: $y = (24.47 \pm 2.07)x + 4.50 \pm 0.92$; $r = 0.9826$.





Peak	Position (1/100)	Height (%)	Area	Area (%)
1	17.91	2.43	0.2929	5.60
2	24.60	3.54	0.4114	7.87
3	31.82	4.07	0.4377	8.38
4	39.30	3.83	0.4816	9.22
5	47.06	4.40	0.5559	10.64
6	54.55	4.02	0.5022	9.61
7	61.50	4.73	0.6317	12.09
8	69.25	4.73	0.7089	13.57
9	77.81	3.67	0.4517	8.64
10	86.10	5.38	0.7514	14.38

Fig. 3. Analysis of a dilute aged solution of perbromate. Top: Calibration curve. Perbromate: $y = (0.58 \pm 0.03)x + 3.23 \pm 0.38$; $r = 0.9942$. Bromate: $y = (3.04 \pm 0.17)x + 3.85 \pm 0.46$; $r = 0.9921$. Densitometer 1 gives the peaks of perbromate as printed out by the software. Spots 2, 6 and 9 are the spots analysed, the other spots are the solutions used for the calibration curve. Densitometer 2 gives the peaks of bromate. The sequence is that of densitometer 1. The average peak for perbromate is 0.92 nmoles and for bromate 0.11 nmoles. The original solution contained 0.1 mmoles in 100 ml and aged for four years.



Peak	Position (1/100)	Height (%)	Area	Area (%)	Quantity
1	17.65	5.11	0.5439	6.74	n/a
2	24.33	5.49	0.6471	8.02	n/a
3	30.75	5.57	0.5627	6.98	n/a
4	39.04	6.75	0.8407	10.42	n/a
5	47.86	7.83	0.9299	11.53	n/a
6	54.28	4.77	0.5202	6.45	n/a
7	60.70	8.23	1.0564	13.10	n/a
8	69.25	9.04	1.2072	14.97	n/a
9	77.54	4.74	0.5165	6.40	n/a
10	85.83	9.06	1.2419	15.40	n/a

Fig. 3 (*continued*).

analysis of an impure sample of potassium perbromate and a dilute solution of potassium perbromate aged for four years at room temperature.

2. Experimental

Merck 5577 thin layers consisting of microcrystalline cellulose were used throughout. Solutions were placed on the thin layers using 1-μl disposable micropipettes (Blaubrand intra End Cat No. 709101).

Volumes of 1μl were spotted on the layers as round spots. Halmilton microsyringes proved unsatisfactory as the metal tip reduces the perbromate rather quickly even in a neutral solution. The developing solvent was prepared by equilibrating 100 ml of butanol puriss p.a. ACS (from Fluka AG, Buchs, Switzerland) with 100 ml dilute ammonia (5 ml conc. ammonia + 95 ml deionised water). Glass jars (8 × 20 cm, height 17 cm) with glass lids were used. The aqueous phase of the solvent was placed in a small beaker in one corner of the jar. As there is a large difference in R_F between potassium perbromate and potassium bromate a short development was adopted, 1–1.5 h; in this period the solvent moves about 6 cm. The plates are then dried with a hairdryer and dipped into a solution of 1% soluble starch and 2% KI in 6 *M* HCl. After ca. 30–60 s the plate is placed under the CCD camera of the Cybertech Gel documentation system WINCAM 2.1 and after focusing a picture is taken. The concentration ranges for quantitation are 0.05–1 nmol for $KBrO_4$ and 0.01–1 nmol for $KBrO_3$.

For the image processing a computer was running the Cybertech WINCAM 2.1 image analysis software. As shown below in Figs. 1–4

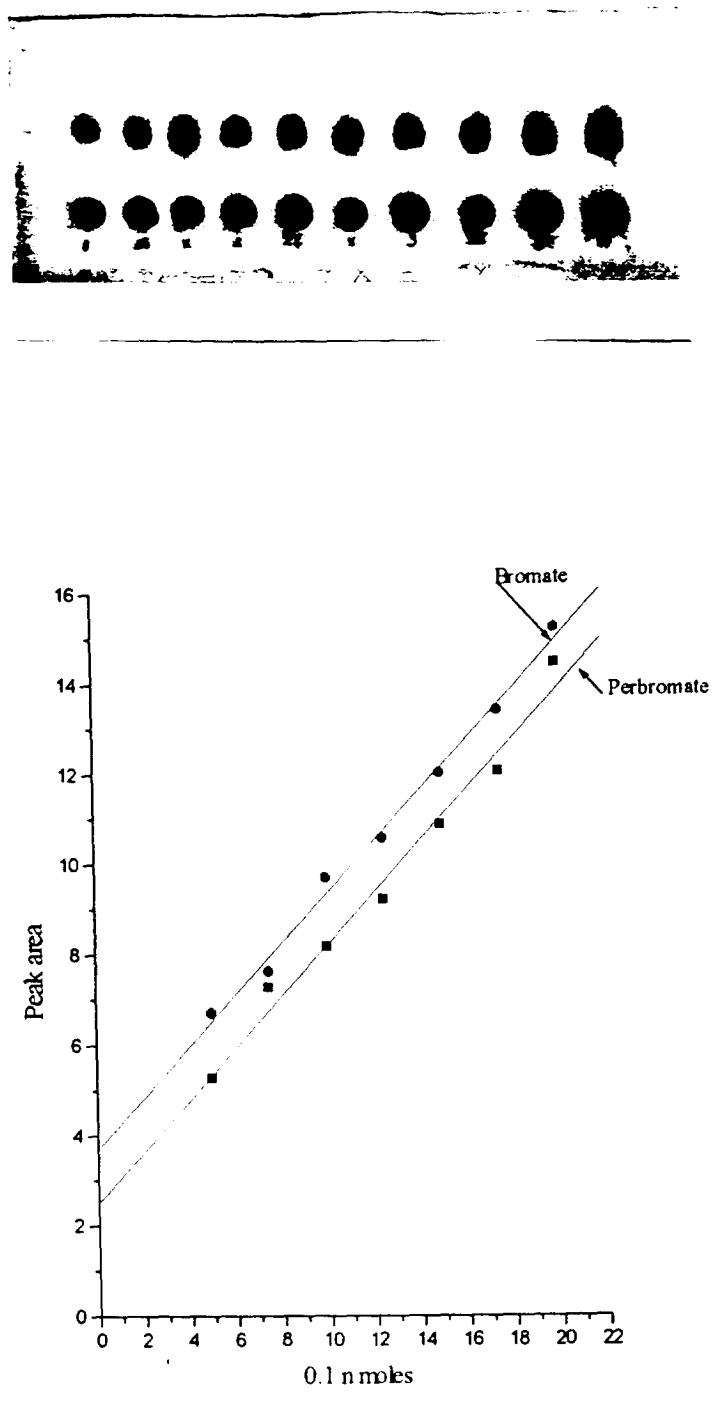
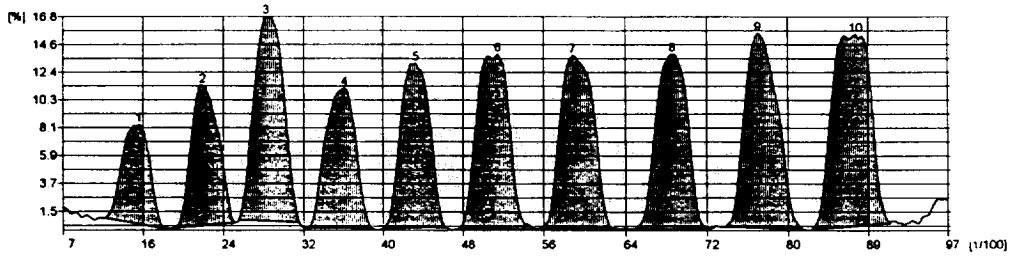


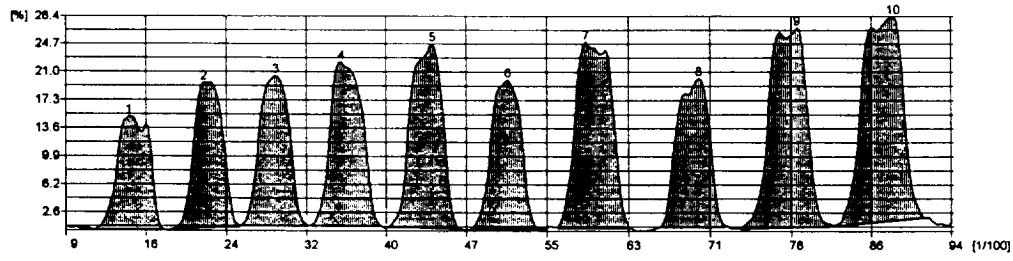
Fig. 4. Analysis of an impure sample of potassium perbromate. From top to bottom: Photo of the developed chromatogram with the CCD camera. Calibration curve. Perbromate: $y = (0.57 \pm 0.03)x + 2.51 \pm 0.45$; $r = 0.9915$. Bromate: $y = (0.56 \pm 0.02)x + 3.70 \pm 0.29$; $r = 0.9965$. Densitometer results for perbromate. Densitometer results for bromate. The sample is in positions 3, 6 and 8. The other spots are the solutions shown in the calibration curve above.

Densitometer: 1



Peak	Position (1/100)	Height (%)	Area	Area (%)
1	15.24	7.80	0.9451	5.27
2	21.66	10.97	1.3024	7.26
3	28.07	16.04	2.0888	11.65
4	36.10	10.97	1.4631	8.16
5	43.32	12.90	1.6478	9.19
6	51.60	13.69	1.9395	10.81
7	59.09	13.60	1.9433	10.84
8	68.98	13.73	1.8600	10.37
9	77.54	15.28	2.1551	12.02
10	87.43	15.03	2.5898	14.44

Densitometer: 2



Peak	Position (1/100)	Height (%)	Area	Area (%)
1	14.97	14.95	2.0285	6.70
2	22.19	19.20	2.3037	7.61
3	29.14	19.76	2.4727	8.17
4	35.56	21.67	2.9304	9.68
5	44.39	24.26	3.1945	10.55
6	51.60	19.65	2.4459	8.08
7	59.09	24.52	3.6329	12.00
8	69.79	19.59	2.6067	8.61
9	79.14	26.34	4.0539	13.39
10	88.50	27.01	4.6000	15.20

Fig. 4 (*continued*).

this yields the integrated peaks, their heights and areas as well as the calibration curve including its statistical evaluation.

Fig. 1 shows the results when perbromate–bromate mixtures of a molar ratio 1:10 were prepared with 0.05 nmol of perbromate and 0.5–3.5 nmol of bromate. Both yield a linear response in this range.

Fig. 2 shows the results with a molar ratio perbromate–bromate of 20:1. Again the response is linear in the range 0.2–1.4 nmol for perbromate and 0.01–0.07 nmol for bromate.

During spotting of the sample the bromate is concentrated on the outer rim of the spots and this produces the two peaked densitometer curves.

For sample analysis 3 spots of the solution to be analysed are placed between the calibration spots. As there are several factors which influence the liberation of iodine from perbromate it is evident that the calibration solution must be run on the same layer as the samples.

Fig. 3 shows the chromatograms obtained with a solution of 18 mg of $KBrO_4$ in deionised water which had been left to stand for four years on a shelf in the laboratory with usual light and temperature variations. The chromatogram yielded a molar ratio of 0.92 nmoles perbromate and 0.11 nmoles bromate. Thus after four years only ca. 10% of the original perbromate had been reduced to bromate.

Fig. 4 is a sample from an improved synthesis made about a year ago. It was an attempt to use the synthesis described by Appelman [4], i.e. oxidation of an alkaline solution of perbromate with gaseous fluorine, and to reduce the number of purification steps of this synthesis. Preliminary qualitative chromatograms had shown that the product contained considerable amounts of bromate. The bromate content was here found to be $37.8 \pm 2.3\%$. In paper and thin-layer chromatography visual examination gives an estimate with an accuracy of $\pm 20\%$. This it is always possible to make a rough check of the results by visual inspection.

References

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