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Title: The Discovery of Electrokinetic Phenomena: Setting the Record Straight

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1 The Discovery of Electrokinetic Phenomena: 2 Setting the Record Straight

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5 Electrokinetic phenomena involve relative tangential motion between a
6 liquid containing ions (e.g. electrolyte solution) and a charged solid surface.
7 Electro-osmosis and electrophoresis are the two most widely studied
8 electrokinetic effects, with a history dating back to the early 1800s.
9 According to IUPAC, electro-osmosis is the electrically driven motion of
10 liquid through a porous solid medium; electrophoresis is the electrical
11 migration of charged colloidal particles or polyelectrolytes immersed in a
12 liquid.^[1] Today, electro-osmosis and electrophoresis are among the most
13 common methods for liquid actuation and particle manipulation,
14 respectively, in microscale analysis systems,^[2–4] with applications including
15 DNA analysis (sizing, genotyping, and sequencing), protein fractionation
16 and analysis, enzyme assays and immunoassays, cell manipulation, forensic
17 science, and chemical synthesis.^[2,4–10] In geotechnology, electro-osmosis and

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18 electrophoresis are applied in the remediation of contaminated soils^[11,12].

19 The story usually goes that electro-osmosis and electrophoresis were
20 discovered by Ferdinand Friedrich Reuss, a German scientist working in
21 Moscow, a little over two centuries ago.^[13–16] There is a twist in the tale,
22 however: although Reuss's landmark 1809 paper^[17] describing his earliest
23 electrokinetics experiments has been widely *cited*, it is evidently much less
24 widely *known*. Table 1 presents an analysis of citations of this paper in 257
25 publications dating from 1901–2016 (see the Supporting Information for
26 further details). Remarkably, and somewhat alarmingly, at least 121
27 distinct forms of citation exist. (The correct citation is given below.) The
28 most common form of citation, which appears in over 30 publications
29 despite apparently originating as recently as 2003,^[18] is disturbingly
30 erroneous, including a fabricated article title, translated journal title, and
31 incorrect volume number and pagination.

32 Taking the vast number of miscitations as a strong indicator that few
33 authors have actually consulted Reuss's paper, one is well entitled to
34 question whether the usual story about the discovery of electrokinetic
35 phenomena is historically accurate. Now that Reuss's once-obscure
36 publications^[17,19] on electrokinetics are freely available online (digitised
37 copies are included in the Supporting Information), the aim of this essay is
38 to address two pertinent questions. Firstly, what exactly did Reuss observe?
39 (This question is answered in detail in the Supporting Information.)
40 Secondly, and more fundamentally, what evidence is there to support the
41 consensus that Reuss *discovered* electrokinetic phenomena?

42 Reuss first encountered electro-osmosis in two experiments that he

Table 1: Analysis of errors in citations of Reuss’s 1809 paper^[17] in 257 publications, of which 133 cite an article title. Several publications contain multiple citation errors.

Citation error	No.	Notes
Author	50	32 omit second initial.
Article title	118	40 omit ‘Notice’ but otherwise give correct title. 41 give fabricated title ‘Charge-induced flow’ or similar.
Journal title	174	42 use variant spellings of ‘Moscou’ but otherwise give correct title. 48 give translated title ‘Proceedings of the Imperial Society of Naturalists of Moscow’ or similar.
Year	18	17 give 1808.
Volume	58	41 give volume 3. 15 omit volume number.
Pagination	85	38 give 327–344.
At least one error	237	Over 92 % of all citations!

43 performed in 1807.^[17,19] A detailed description of these experiments is
 44 provided in the Supporting Information. In summary, Reuss observed that
 45 when an electric current was passed through water contained in two
 46 compartments separated by a porous barrier—either a plug of quartz
 47 powder or a block of moist clay—a flow of water occurred from the anode
 48 to the cathode. In the second experiment, there was also a transfer of clay
 49 particles towards the anode, which most authors attribute to
 50 electrophoresis,^[14] although Reuss himself believed that the effect was due
 51 to electro-osmotic penetration of water into the clay block. Reuss initially
 52 communicated these findings to the Physico-Medical Society of Moscow in
 53 November 1807 in an unpublished lecture entitled ‘Indicium de novo
 54 h[u]cusque nondum cognito effectu electricitatis galvanicae’ (‘Notice on a
 55 new, hitherto unknown effect of galvanic electricity’).^[20] Subsequent

communications were made to the Imperial Society of Naturalists of
 Moscow in April 1808,^[17] published in French as

F. F. Reuss, Notice sur un nouvel effet de l'électricité
 galvanique, *Memoires de la Société Impériale des Naturalistes de*
Moscou **1809**, 2, 327–337,^[21]

and again to the Physico-Medical Society of Moscow in October 1817,^[19]
 published in Latin as

F. F. Reuss, Electricitatis Voltanae potestatem hydragogam
 tanquam novam vim motricem, a se detectam, denuo proposuit
 ejusque in naturae operibus partes investigare tentavit,
Commentationes Societatis Physico-Medicae, apud
Universitatem Literarum Caesaream Mosquensem institutae
1821, 2(2), 307–326.

Despite the significance of the results contained within, these two papers—
 published in Russia in relatively obscure journals—went almost completely
 unnoticed by the wider scientific community for several decades.

The singular ‘nouvel effet’ (new effect) of the electric current referred to
 by Reuss in the title of his 1809 paper^[17] is unquestionably electro-osmosis,
 not electrophoresis. This conclusion is supported by two pieces of evidence.
 Firstly, as mentioned above, Reuss apparently did not consider the possibility
 that the clay in his second experiment could, like the water, be acted upon by
 the electric field. Secondly, the list of four numbered results that conclude his
 paper (given in translation in the Supporting Information) all relate to the
 liquid motion observed in the two experiments. Reuss was certainly qualified

80 to recognise electro-osmosis as a new discovery, having previously authored
81 a review on the chemical effects produced by electricity (particularly the
82 electrolytic decomposition of water).^[22] Further supporting his claim is the
83 fact that electro-osmosis was still considered to be previously unknown when
84 the independent observations of Porrett were published seven years later (see
85 below).

86 Electro-osmosis was independently discovered by the English chemist
87 Robert Porrett Jun. in late 1814 or early 1815.^[23] Porrett's experiments
88 were essentially similar to Reuss's except that a bladder membrane was
89 used as the porous barrier. (Further details, along with a digitised copy of
90 Porrett's paper, are provided in the Supporting Information.) The historical
91 significance of Porrett's 'curious galvanic experiments' is that unlike Reuss's
92 largely neglected work, they were well known to contemporary
93 experimentalists.^[24–30] Furthermore, his choice of a bladder membrane
94 ultimately inspired the term 'electro-osmosis'. Henri Dutrochet, who also
95 worked with bladder membranes in his studies on ordinary osmosis,^[31]
96 noted an apparent analogy between ordinary osmosis (then known as
97 endosmose) and Porrett's description of electrically driven water flow.^[26]
98 Although Dutrochet later abandoned the idea that ordinary osmosis might
99 be an electrical effect,^[32] the analogy proved to be sufficiently resilient that
100 the phenomenon that Porrett had called 'electro-filtration' soon came to be
101 known as 'electrical endosmose'.

102 Contrary to what is often suggested, Reuss did not discover
103 electrophoresis (nor did he claim to have done, as has already been
104 highlighted). In 1801, six years before Reuss's experiments, the French

105 chemist Nicolas Gautherot observed electrophoresis occurring in a drop of
106 water confined between two electrically connected metal plates.^[33] (See the
107 Supporting Information for more details and a digitised copy of Gautherot's
108 paper.) Gautherot's observation of electrophoresis was noted by Humphry
109 Davy in his 1806 Bakerian Lecture^[34] but otherwise seems to have escaped
110 attention. Whether or not Gautherot *discovered* electrophoresis remains
111 unclear, but if he was not the first, he must certainly have been among the
112 first to observe the phenomenon given that the voltaic pile (the first source
113 of steady electric current) had only been introduced in the previous year.^[35]

114 The discovery of electrophoresis is sometimes identified^[36,37] with the
115 discovery by Bose during the 1740s of electrically induced liquid
116 atomisation,^[38] the phenomenon at the centre of the modern electrospray
117 process.^[39] This conflation is based on an uncommonly broad definition of
118 electrophoretic phenomena as being 'those motion phenomena which arise
119 from the direct coulombic action of an electric field on unneutralized charge
120 contained in matter'.^[40] According to the more usual definition
121 recommended by IUPAC (given in the opening paragraph), electrophoresis
122 involves electrical migration of colloids in liquids and therefore has little to
123 do with the atomisation effect discovered by Bose.

124 This essay has outlined the important contributions of three scientists
125 to the discovery of electrokinetic phenomena. The evidence presented herein
126 supports the prevailing consensus that Reuss discovered electro-osmosis in
127 1807. But it is a scarcely known fact that Gautherot observed electrophoresis
128 in 1801, six years before Reuss did. Porrett's contribution is today reflected
129 (if indirectly) in the term 'electro-osmosis'. With the record now thus set

130 straight, it is high time that the germinal publications of these three scientists
131 are appropriately recognised for their historical significance and are correctly
132 cited.

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- [21] Citation taken from the original source volume. Note in particular that the word ‘Notice’ is part of the article title, as confirmed by (i) the entry for this article in the table of contents (p. 356 of the same volume) and (ii) comparison with the title of Reuss’s unpublished lecture from 1807 (cited in the text), on which this article is evidently based. Also note that no acute accent is used in ‘Memoires’ in this volume of the journal, and that ‘Moscou’ is spelt thus.
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Abstract/Table of contents entry

Electro-osmosis and electrophoresis were discovered by F. F. Reuss in Moscow in 1807. Or so the story goes. This essay critically examines the contributions of three scientists to the discovery of electrokinetic phenomena. The evidence suggests that Reuss did indeed discover electro-osmosis, which takes its name (indirectly) from the work of Porrett. Contrary to current consensus, Gautherot made the earliest known observation of electrophoresis.

Keywords: electrokinetics; electro-osmosis; electrophoresis; history of science

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