

ENCYCLOPEDIA
— OF —
SEPARATION
SCIENCE



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ENCYCLOPEDIA OF SEPARATION SCIENCE

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58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.115	140.908	144.24	145	150.36	151.965	157.25	158.925	162.50	164.930	167.26	168.934	173.04	174.967

★ Lanthanoid series

90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232.038	231.036	238.029	237.048	244	243	247	247	251	252	257	258	259	260

▲ Actinoid series

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Group IA	IIA	IIIA	IIIA	IVA	VIA	VIA	VIA	VIA	VIA	IB	IIB	IIIB	IIIA	IVB	VIB	VIIA	VIIIA
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H	He	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar
1.00794	4.00260	6.941	9.01218	10.811	12.011	14.0067	15.9994	18.9984	20.1797	22.9898	24.3050	26.9815	28.0855	30.9738	32.066	35.4527	39.948
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.0983	40.078	44.9559	47.88	50.9415	51.9961	54.9380	55.847	58.9332	58.69	63.546	65.39	69.723	72.61	74.9216	78.96	79.904	83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
85.4678	87.62	88.9059	91.224	92.9064	95.94	(98)	101.07	102.906	106.42	107.868	112.411	114.82	118.710	121.75	127.60	126.905	131.29
55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
132.905	137.327	138.906	178.49	180.948	183.85	186.207	190.2	192.22	195.08	196.967	200.59	204.383	207.2	208.980	(209)	(210)	(222)
87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	105
(223)	226.025	227.028	232.038	231.036	238.029	237.048	244	243	247	247	251	252	257	258	259	260	(261)

Periodic Table of the Elements

ENCYCLOPEDIA OF SEPARATION SCIENCE

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Foreword

Separation science was first recognized as a distinct area of physical and analytical chemistry in the 1960s. The term was first coined, I believe, by the late J. Calvin Giddings, Research Professor at the University of Utah. Calvin Giddings recognized that the same basic physical principles governed a wide range of separation techniques, and that much could be learnt by applying our understanding of one such technique to others. This was especially true for his first loves, chromatography and electrophoresis and latterly field flow fractionation. Of course there are many separation techniques other than chromatography, many with a history at least as long, or indeed longer, than that of chromatography: distillation, crystallization, centrifugation, extraction, flotation and particle separation, spring to mind. Other separation techniques have emerged more recently: affinity separations, membrane separations and mass spectrometry. Most people, a few years ago, would not have classed mass spectrometry as a separation technique at all. However, with modern ionization methods, which minimize fragmentation, mixtures of compounds can first of all be separated and then each component identified through fragmentation by secondary ion-molecule collisions and further mass spectrometry. With the scale of mass spectrometry now matching that of microseparation methods such as capillary electrophoresis and capillary electrochromatography, combinations of orthogonal methods can now provide extremely powerful separation and identification platforms for characterizing complex mixtures.

Basically, all separation techniques rely on thermodynamic differences between components to discriminate one component from another, while kinetic factors determine the speed at which separation can be achieved. This applies most obviously to distillation, chromatography and electrophoresis, but is also obvious in most of the other techniques; even particle size separation by sieving can be classified in this way. The thermodynamic aspect is, of course, trivial being represented by the different sizes of the particles, as indeed it is for the size exclusion chromatography of polymers. However, the kinetic aspects are far from trivial. Anyone who has tried to sieve particles will have asked the question: is it better to fill the sieve nearly to the top and sieve for a long time, or is it better to dribble the material slowly into the sieve and just remove the heavies from time to time? One might further ask: how does one devise a continuous sieving process where large particles emerge from one port of the equipment, and small ones emerge from the other port? And how does one optimize throughput and minimize unit cost?

The publication of this *Encyclopedia of Separation Science* is a landmark for this area of science at the start of the third millennium. It will undoubtedly be of enormous value to practitioners of separation science looking for an overview and for guidance as to which method to select for a new problem, as well as to those who are at an early stage, simply dipping their toes into the waters, and trying to find out just what it is all about. Most important of all, by providing a comprehensive picture, it advances the whole field of separation science and stimulates further work on its development and application. The publishers, their editors and their authors are to be congratulated on a splendid effort.



John H. Knox
Edinburgh
8 March 2000

Preface

The ability to perform separations for the analysis, concentration or isolation of substances present in mixtures (of varying degrees of complexity) is arguably fundamental to the maintenance of our technological civilization. Separations can also be rather difficult to define, and over the course of a number of debates where we tried to 'separate the wheat from the chaff', we defined separations for the purposes of this work as '*processes of any scale by which the components of a mixture are separated from each other without substantial chemical modification*'. Of course some of the processes that are used in separations have a very long history, and the terms used to describe them are in widespread general use. So, we talk about how it is possible to distil wisdom, precipitate an argument, extract meaning and crystallize an idea and who can predict the future uses of the word chromatography? Whilst separations have been practised as an *art* for millennia, the last hundred years or so has seen the elucidation of the fundamentals that lie behind many of these processes. Thus, although separations are most widely used for achieving some practical objective, a firm theoretical understanding has been put into place that does allow the use of the term *separation science*. We have tried here to reflect the theoretical and practical aspects of the topics in this encyclopedia, and have attempted to achieve a blend of theory, practice and applications that will enable someone knowledgeable in a field to go directly to a relevant article; whilst the novice can begin with an overview and gradually iterate towards the practical application.

One thing is clear, separations cover such a wide range of topics that no single individual can be knowledgeable, let alone expert, in them all. It is against this background that we decided that an encyclopedia designed to cover this science would be of value as a single source of reference that would provide access to the whole field of separations.

For the purposes of defining the scope and coverage of the encyclopedia we have divided the area of separations into 12 families, or topic areas, using separation principles based on affinity, centrifugation, chromatography, crystallization, distillation, electrophoresis, extraction, flotation, ion exchange, mass spectrometry, membranes and particle size. Whilst there is no doubt that different editors might have grouped these slightly differently, they did not seem to us to be capable of further reduction. Taken together, we believe that they provide coverage of the whole field.

In preparing this multi-author and multi-volume work, all of the editors have been conscious of the gaps in their own expertise and the debt which they and the publishers owe to the Editorial Advisory Board, who to a large degree have compensated for the deficiencies in our own knowledge. Their help has been invaluable, as without them we would not have been able to achieve the necessary balance and it was, therefore, a source of particular sadness that one of them, Ted Woodburn, died prior to publication. Without Ted it is quite clear that the topic area of flotation would not have been so well covered, and we would like to think that he would have been well pleased with the finished work. We also hope that the masterly overview which he contributed to the encyclopedia, will be a lasting memorial to him. We are grateful to Jan Cilliers for stepping into the role of Editorial Board Advisor on flotation at short notice. We would also like to acknowledge the valuable input of G. J. Arkenbout at the beginning of this project, who was able to work with us for a short period of time before his death.

Assembling this knowledgeable and enthusiastic group of experts was a difficult task, and the editors would also wish to acknowledge the role of the Major Reference Works development team at Academic Press in this whole area, as well as thanking them for their assistance and patience throughout the project, from the initial planning to its final publication.

Finally, of course, we must acknowledge the contributions of the authors whose expertise constitutes this encyclopedia. Some of them have become firm friends in the period between the inception of this project and its completion. After all, separation science separates things but brings people together.

Ian D. Wilson, Edward R. Adlard, Michael Cooke, Colin F. Poole
Editors

Introduction

The need for separations as a means for performing the isolation, purification or analysis of substances, at scales ranging from tonnage quantities down to picograms or less, is an important feature of modern life. Such separations underpin virtually all aspects of research and commerce and indeed a vast industry has arisen to provide the equipment and instrumentation to perform and control these essential processes; indeed it is impossible to envisage our world without ready access to separations. To provide these capabilities a whole family of techniques has evolved to exploit differences in the physical or chemical properties of the compounds of interest, and to accommodate the scales on which the separations are performed. After all, a separation that works on the picogram scale based perhaps on capillary electrophoresis, may not easily be transferred to the gram scale and will be utterly impossible on the kilogram scale. In such instances an alternative type of separation, based on a totally different principle must be sought. And therein lies the problem—most scientists are specialists and while having an excellent knowledge of their own, often narrow, sphere of expertise are generally possessed of a much more hazy view of the capabilities and attributes of techniques outside that area. Even worse, such ignorance may persuade them to adopt an approach that is quite unsuited to the solution of the problem in hand.

The large number of articles in this encyclopedia, and the wide variety of the subject matter described in them, represents an attempt to provide separation scientists with a single authoritative source covering the broad range of separation methods currently available. Inevitably there is some overlap in places between articles dealing with closely related topics. However, in a work such as this where each article is meant to be a self-contained source of information, some overlap is unavoidable and not wholly undesirable in the context of ensuring full coverage of a topic.

The articles in the *Encyclopedia of Separation Science* fall into three categories as follows: 'Level I', which provides overviews of a particular separation area, e.g. flotation, distillation, crystallization, etc., written by acknowledged experts in the particular fields. These articles are presented with the aim of providing a wide ranging introduction to the topic from which the reader can then, if it seems appropriate, move on to 'Level II' articles.

Level II articles cover the theory, development, instrumentation and practice of the various techniques contained within each broad classification. For example the Level I article on chromatography is supported in Level II by descriptions of gas, liquid and supercritical fluid chromatography, together with information on instrumentation. Separations are, however, often of interest to practitioners because of their applications and Level II serves as an introduction to 'Level III'.

Level III provides detailed descriptions of the use of the various methods described in Levels I and II for solving real problems. These might include articles on the various methods for extraction of pesticides or drugs from a matrix, with other articles on the chromatographic or electrophoretic techniques that could be used for their subsequent analysis. The extensive cross-referencing and exhaustive indexing for all of the articles in the work should enable the reader to obtain easily and rapidly all the relevant information in the encyclopedia. In addition, each article at whatever level contains a brief but carefully selected bibliography of key books, review articles and important papers. In this way the encyclopedia provides the reader with an invaluable 'gateway' into the separation science literature on a topic.

Lastly, because the importance of separation science lies in its value as an applied technique, we have commissioned a number of 'essential guides' to method development, in a limited number of key areas such as the isolation and purification of proteins and enzymes, etc., or the development of chromatographic separations.

While the techniques described in these volumes can in many cases be used as the basis of analytical methods, the emphasis of this work is on the methods of separation of mixtures, rather than their determination. For a treatise devoted to Analytical Science the reader is referred to the *Encyclopedia of Analytical Science*, also published by Academic Press, which can be considered to be complementary to the present work, in that it deals in depth with analysis rather than the application of separations.

The reader faced with the need to perform a separation, requiring information on a type of detector, or the use of a technique for a particular class of compound, etc., should therefore be able to look into the encyclopedia for information on that topic. Even where there is no information that is directly relevant to

the problem, it should still be possible to begin at Level I in order to determine the potential of a technique to solve the problem and then progress down through the levels until a solution begins to emerge.

The editors believe that, taken as a whole, this encyclopedia and its electronic version should provide a valuable source of knowledge and expertise for both those already skilled in the art of some aspect of separations and also for the novice. That, at least, is our hope.

This encyclopedia is a guide providing general information concerning its subject matter; it is not a procedure manual. The readers should consult current procedural manuals for state-of-the-art instructions and applicable government safety regulations. The publisher and the authors do not accept responsibility for any misuse of this encyclopedia, including its use as a procedural manual or as a source of specific instructions.

Guide to Use of the Encyclopedia

Structure of the Encyclopedia

The material in the encyclopedia comprises a series of entries on three levels, as follows:

- Level I entries, 'Overviews', provide broad overviews of the separation techniques covered by the encyclopedia, and comprise 12 single articles, arranged alphabetically.
- Level II entries, 'Methods and Instrumentation', provide detailed theoretical and technical descriptions of separation techniques. Entries for each separation technique are listed under the broad heading for each, with the latter following, in alphabetical sequence. Entries may consist of either single articles or several articles that deal with various aspects of the topic. In the latter case the articles are arranged in a logical sequence within their technique headings, for example:

ION EXCHANGE:

Catalysis: Organic Ion Exchangers

Historical Development

Inorganic Ion Exchangers

Multispecies Ion Exchange Equilibria *See Ion Exchange: Surface Complexation Theory: Multispecies Ion Exchange Equilibria.*

Non-Phosphates: Novel Layered Materials *See Ion Exchange: Novel Layered Materials: Non-Phosphates.*

Novel Layered Materials: Phosphates

Novel Layered Materials: Non-Phosphates

Organic Ion Exchangers

Organic Membranes

Phosphates: Novel Layered Materials *See Ion Exchange: Novel Layered Materials: Phosphates.*

Surface Complexation Theory: Multispecies Ion Exchange Equilibria

Theory of Ion Exchange

- Level III entries, 'Practical Applications', (comprising single or multi-article entries) describe applications of these separation techniques to particular separation problems, and are arranged in alphabetical sequence.

To help you realize the full potential of the material in the encyclopedia we have provided the following features to help you find the topic of your choice.

1. Contents List

Your first point of reference will probably be the contents list. The complete contents list appearing in each volume will provide you with both the volume number and page number of the entry. On the opening page of an entry a contents list is provided so that the full details of the articles within the entry are immediately available.

Alternatively you may choose to browse through a volume; to assist you in identifying your location within the encyclopedia a running headline indicates the current level, the current entry and the current article within that entry.

You will find 'dummy entries' where obvious synonyms exist for entries or where we have grouped together related topics. Dummy entries appear in both the contents list and the body of the text. For example a dummy entry appears within Level II for Membrane Separations: Kidney Dialysis which directs you to **Membrane Separations: Dialysis in Medical Separations**, where the material on this subject is located.

Level II Example

If you were attempting to locate material on Polyacrylamide Gel Electrophoresis via the Electrophoresis section, you could do this either via **A** the contents list, or **B** browsing through the text.

A The contents list

ELECTROPHORESIS (*Continued*)

One-dimensional Sodium Dodecyl Sulfate Polyacrylamide Gel Electrophoresis

Polyacrylamide Gel Electrophoresis *See* ELECTROPHORESIS: Two-dimensional Polyacrylamide Gel Electrophoresis, ELECTROPHORESIS: One-dimensional Sodium Dodecyl Sulfate Polyacrylamide Gel Electrophoresis, ELECTROPHORESIS: One-dimensional Polyacrylamide Gel Electrophoresis.

Porosity Gradient Gels

Proteins, Detection of

Staining *See* ELECTROPHORESIS: Detection Techniques: Staining, Autoradiography and Blotting

Theory of Electrophoresis

Two-dimensional Electrophoresis

Two-dimensional Polyacrylamide Gel Electrophoresis

At the appropriate location in the contents list, the page numbers for these articles are given.

B Browsing through the text

If you were trying to locate the material by browsing through the text and you looked up Electrophoresis: Polyacrylamide Gel Electrophoresis then the following information would be provided.

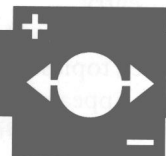
ELECTROPHORESIS: POLYACRYLAMIDE GEL ELECTROPHORESIS

See II/ELECTROPHORESIS: One-dimensional Polyacrylamide Gel Electrophoresis; One-dimensional Sodium Dodecyl Sulfate Polyacrylamide Gel Electrophoresis; Two-dimensional Polyacrylamide Gel Electrophoresis

Alternatively, if you were looking up Electrophoresis: One-dimensional Polyacrylamide Gel Electrophoresis the following information would be provided. The icon that appears alongside the article title indicates which of the 12 main areas of separation the article falls within.

ELECTROPHORESIS/One-Dimensional Polyacrylamide Gel Electrophoresis

ELECTROPHORESIS



One-Dimensional Polyacrylamide Gel Electrophoresis

Level III Example

If you were attempting to locate material on Aromas, you could do this either via **A** the contents list, or **B** browsing through the text.

A The contents list

Aromas: Gas Chromatography* *See* Fragrances: Gas Chromatography

*Note articles are arranged alphabetically within each entry.

At the appropriate location in the contents list, the page numbers for these articles are given.

B Browsing through the text

If you were trying to locate the material by browsing through the text and you looked up Aromas then the following information would be provided.

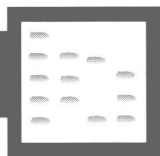
AROMAS: GAS CHROMATOGRAPHY

See III/Fragrances: Gas Chromatography

Alternatively, if you were looking up Fragrances the following information would be provided. The icon that appears alongside the article title indicates which of the 12 main areas of separation the article falls within.

FRAGRANCES: GAS CHROMATOGRAPHY

FRAGRANCES: GAS CHROMATOGRAPHY



2. Cross References

All of the articles in the encyclopedia have been extensively cross-referenced. These include 'see' cross references that are located within the text of each article that direct the reader to articles which are of immediate relevance to the topic. 'See also' cross-references appear at the end of the article, and point to related topics. These take the following form:

- i. To indicate where a topic is discussed in greater detail elsewhere.

III/AMINO ACIDS AND DERIVATIVES: CHIRAL SEPARATIONS

See also: II/Chromatography: Liquid: Derivatization. III/Chiral Separations: Capillary Electrophoresis; Cellulose and Cellulose Derived Phases; Chiral Derivatization; Countercurrent Chromatography; Crystallization; Cyclodextrins and Other Inclusion Complexation Approaches; Gas Chromatography; Ion-Pair Chromatography; Ligand Exchange Chromatography; Liquid Chromatography; Molecular Imprints as Stationary Phases; Protein Stationary Phases; Synthetic Multiple Interaction ('Pirkle') Stationary Phases; Supercritical Fluid Chromatography; Thin-Layer (Planar) Chromatography.

- ii. To draw the reader's attention to parallel discussions in other articles.

III / AMINO ACIDS AND DERIVATIVES: CHIRAL SEPARATIONS

See also: **II/Chromatography: Liquid:** Derivatization. **III/Chiral Separations:** Capillary Electrophoresis; Cellulose and Cellulose Derived Phases; Chiral Derivatization; Countercurrent Chromatography; Crystallization; Cyclodextrins and Other Inclusion Complexation Approaches; Gas Chromatography; Ion-Pair Chromatography; Ligand Exchange Chromatography; Liquid Chromatography; Molecular Imprints as Stationary Phases; Protein Stationary Phases; Synthetic Multiple Interaction ('Pirkle') Stationary Phases; Supercritical Fluid Chromatography; Thin-Layer (Planar) Chromatography.

- iii. To indicate material that broadens the discussion.

III / AMINO ACIDS AND DERIVATIVES: CHIRAL SEPARATIONS

See also: **II/Chromatography: Liquid:** Derivatization. **III/Chiral Separations:** Capillary Electrophoresis; Cellulose and Cellulose Derived Phases; Chiral Derivatization; Countercurrent Chromatography; Crystallization; Cyclodextrins and Other Inclusion Complexation Approaches; Gas Chromatography; Ion-Pair Chromatography; Ligand Exchange Chromatography; Liquid Chromatography; Molecular Imprints as Stationary Phases; Protein Stationary Phases; Synthetic Multiple Interaction ('Pirkle') Stationary Phases; Supercritical Fluid Chromatography; Thin-Layer (Planar) Chromatography.

3. Index

The index in Volume 10 will provide you with the volume number and page number showing where the material is located. The index entries differentiate between material that is a whole article, is part of an article or contains data presented in a table. On the opening page of the index detailed notes are provided.

4. Colour Plates

The colour figures for each volume have been grouped together in a plate section. The location of this section is cited both in the contents list and before the *See also* list of the pertinent articles.

5. Appendices

In addition to the articles that form the main body of the encyclopedia, you will find material in the appendices that provides 'Essential Guides' to topics such as method development in a particular separation technique, IUPAC definitions of chromatographic terms and conventions, and a range of tabulated material providing physical constants.

The Appendices are located in Volume 10.

6. Contributors

A full list of contributors appears in Volume 10.

★ Lanthanoid series	58 Ce 140.115	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
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▲ Actinoid series	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)
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1 Group IA	2	New notation Previous IUPAC form CAS version										13	14	15	16	17	18 VIIIA
1 H 1.00794	2 He 4 9.01218	3 Li 6.941	4 Be 9.01218	5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797	11 Na 22.9898	12 Mg 24.3050	13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.82	50 Sn 118.710	51 Sb 121.75	52 Te 127.60	53 I 126.905	54 Xe 131.29
55 Cs 132.905	56 Ba 137.327	57 La 138.906	58 Ce 140.115	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967	72 Hf 178.49
87 Fr (223)	88 Ra 226.025	89 Ac 227.028	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)	104 Rf (261)
																	105 Ta 180.948
																	106 W 183.85
																	107 Re 186.207
																	108 Os 190.2
																	109 Ir 192.22
																	110 Pt 195.08
																	111 Au 196.967
																	112 Hg 200.59
																	113 Tl 204.383
																	114 Pb 207.2
																	115 Bi 208.980
																	116 Po (209)
																	117 At (210)
																	118 Rn (222)

Periodic Table of the Elements