Contributions to the new one step S19®online method for the extraction and isolation of pesticide residues and environmental chemicals

4. The pioneering results and facts of the online S19® extraction method

Einleitung

In den drei vorhergehenden Beiträgen 1-3 dieser Publikationsserie(7, 9, 12) wurde die neue einstufige und bahnbrechende S19®online Extraktionsmethode(1), sowohl in der Mikro- und Makroausführung beschrieben. Zur Extraktion diente ein binäres und ternäres Lösungsmittelsystem, mit Aceton als polares Lösungsmittel.

Bedauerlicherweise wurde diese bahnbrechende online Extraktionsmethode(1) seit ihrer Publikation im Jahre 1985 mehrmals plagiiert.

Diese „Autoren" anerkannten zwar die großen Vorteile dieser neuen universellen online Methode gegenüber den alten offline Methoden, wie z. B. der Specht et al Methode, insbesondere was die Zeitersparnis, den Gebrauch von nicht toxischen Lösungsmittel, den Gebrauch von Mikro Extraktionsmethoden und der Einfachheit der Handhabung betrifft(siehe Punkt1-19), unterließen es jedoch darauf hinzuweisen, daß die online Extraktionsmethode, die sie beschrieben, die seit den späten Achziger Jahren international anerkannte online Methoden von H. Steinwandter ist(1-18).

Andere „Autoren" wiederum, nämlich W. Gilsbach, W. Specht, J. Siebers, beanspruchten jedoch diese Methode allen Ernstes noch bis heute für sich.

Der Grund für den Anspruch z. B. für Gilsbach ist u. a. seine Behauptung(Schreiben v. 24. 3. 2000), daß er die Phasentrennung der im Jahre 1985 publizierten universellen online Methode von Steinwandter 10 Jahre später, also im Jahre 1995 „**zufällig**" entdeckt hätte. W. Gilsbach berichtete u. a. weiter, daß er über das Ergebnis der Phasentrennung so überrascht war, daß er die Extraktion „**willentlich**" wiederholte.

Dieser Anspruch von Gilsbach ist aber umso unverständlicher, als ein Mitarbeiter von W. Gilsbach im Jahre 1993 an einem praktischen Fortbildungskurs(Mikro Methodenkurs) in den **Laboratorien von H. Steinwandter** teilnahm, bei dem alle bekannten Vorteile der

universellen online Extraktionsmethode(1-18) gegenüber allen konventionellen offline Verfahren(19-23) praktisch demonstriert wurden(17,18).

Herr Gilsbach bekam also alle Ergebnisse des Kurses mundgerecht vorgelegt.

Wie man sieht, ist diese moderne Version der **Wissenschaft „made in germany",** praktiziert von W. Gilsbach, eher eine Posse.(siehe H. Steinwandter,Counter-statement, Fresenius J Anal chem(1996) 353: 183)

Was die Evolution der bahnbrechenden universellen S19®online Extraktionsmethode von Steinwandter betrifft, ist es wichtig festzustellen, daß bis zur Entwicklung dieser bahnbrechenden universellen online Methode im Jahre 1985, alle Ergebnissen, die mit den bisherigen konventionellen offline Extraktionsmethoden(19-23) ermittelt wurden, prinzipiell falsch waren. Der Grund hierfür war, daß mit diesen Methoden die Analysenergebnisse auf den unbekannten also nicht gemessenen Wassergehalt der filtrierten Aceton-bzw. Acetonitrilextrakte normiert waren. Während jedoch Mills et al und Luke et al den Betrag dieses geschätzten Wassergehaltes als solchen verwendeten, gingen Specht et al, die die Methode von Luke et al entlehnten, anders vor. Diese Autoren verwendeten ebenfalls den geschätzten Wassergehalt zur Berechnung der Analysenergebnisse, täuschten aber ein genaueres Ergebnis vor, indem sie die unbekannte Wassermenge der Probe durch Zusatz einer entsprechenden Wassermenge auf eine exakte Größe, z. B. 100 g einstellten. Es wurde also eine unbekannte Größe mit einer weiteren unbekannten Größe auf eine vorgetäuschte genaue Größe(100g) eingestellt!

Das Endergebnis war aber hier wie dort auf den unbekannten also nicht gemessenen Wassergehalt der Probe normiert. Folglich war des Endergebnis ebenfalls nur ein Schätzwert und daher falsch.

Im Jahre 1985 konnte diese bestürzende Situation durch die Entwicklung der bahnbrechenden universellen S19®online Extraktionsmethode beseitigt werden, da das Analysenergebnis nunmehr nicht mehr auf eine unbekannte sondern auf eine bekannte Größe, nämlich, auf das Gesamtvolumen der genau abgemessenen und zugesetzten polaren und unpolaren Lösungsmittel normiert wurde.

Bei dieser neuen universellen S19®online Technik wurde die unbekannte Wassermenge der Probe in einem einzigen Schritt vom polaren und unpolaren Lösungsmittel abgetrennt werden, so daß schließlich eine Wasserphase und eine reine organische Phase erhalten wurden. Diese organische Phase bestand somit aus den verwandten polaren und unpolaren Extraktions-mitteln, deren Mengen bzw. Volumina für die Extraktion genau abgemessen wurden, sodaß die Endergebnisse auf diese normiert und dadurch erstmals präzise Analysenergebnisse erhalten werden konnten.

Durch die neue universelle S19®online Technik konnten auch **erstmals alle Acetonitril-und Acetonmethoden zu einer einzigen universellen S19®online Extraktionsmethode vereinheitlicht werden.**

Die bahnbrechenden Vorteile der universellen S19®online Extraktionsmethode gegenüber allen anderen konventionellen offline Verfahren sind:

1. Alle Arbeitsschritte werden im selben Extraktionsgefäß in einem einzigen Schritt durchgeführt,

2. Zusätzlich zum simultanen Schritt und zu den einzelnen möglichen sequentiellen Schritten kann auch jede beliebige Kombination beider Systeme verwandt werden,

3. Keine Filtration der Probenextrakte nach der Acetonitril- oder Acetonextraktion ist notwendig,

4. Kein Aliquot des Probenextraktes nach der Filtration ist notwendig,

5. Kein Scheidetrichter für den Verteilungsschritt ist notwendig,

6. Kein Scheidetrichter für die Abscheidung des Wassers aus dem Probenextrakt ist notwendig,

7. Das Volumen der organischen Phase ist unabhängig vom Wassergehalt der Probe

8. Das Volumen der organischen Phase setzt sich aus der Summe des verwendeten Volumens des polaren und unpolaren Lösungsmittels zusammen,

9. Die Wassermenge der Probenextraktes hat zum ersten Male keinen Einfluß auf das Analysenergebnis,

10. Ein Minimum von Extraktionsschritten führt zu einem Minimum von analytischen Fehlern,

11. Ein Minimum von Glasgeräten ist notwendig

12. Die Extraktion der neuen universellen S®19 Extraktionsmethode von H. Steinwandter ist nach 10 sec beendet, in einigen Fällen nach 1-2 sec,

13. Sofortige Phasentrennung,

14. Die universelle S19®online Technik kann durch die Steinwandter Diagramme dargestellt werden,

15. Mit der neuen S19®online Methode wurden über 400 Pestizide und Umweltchemikalien untersucht, mit Wiederfindungen von 80 bis 100%,

16. In 14 Jahresberichten der Hessischen Landwirtschaftlichen Versuchsanstalt Darmstadt wurden die Fortschritte und Entwicklungen der neuen S19®online Extraktionsmethode ausführlich berichtet,

17. Die neue S19®online Extraktionsmethode wurde in Vorträgen, auf Kongressen und in Frühjahrstagungen vorgestellt,

18. Durch die neue S19®online Technik konnten **alle Aceton- und Acetonitrilmethoden zu einer einzigen universellen S19®online Extraktionsmethode vereinheitlicht werden**,

19. Die universelle S19®Extraktionsmethode kann, im Gegensatz zu den konventionellen offline Methoden, zum ersten male miniaturisiert werden, sodaß die Lösungsmittel-und Chemikalienmengen gegenüber den offline Methoden um den Faktor 1/10 bis 1/100 reduziert werden konnten.

Die Punkte 1 bis 19 können nur von der universellen S19®online Extraktionsmethode abgleitet werden.

Introduction

In the previous three papers 1-3 of the series(7, 9, 12) the new one step S19®online extraction method(1) in the micro and macro mode using the binary and ternary solvent system with acetone as the polar solvent was described in detail.

Unfortunately, since the publication in 1985 the pioneering universal S19®online extraction method(1) was plagiated several times.

These „authors" recognized of course the great advantages of the universal online extraction method for the extraction of pesticides in terms of time saving, use of nontoxic solvents, use of micro methods, ease of handling and so on(see points 1 through 19)when compared to the old offline extraction method e. g. of Specht et al, but they omitted to mention, that the extraction method they described is the universal online method(1), recognized world wide since the late eighties(1-18).

Some of these „authors", W. Gilsbach, W. Specht, J. Siebers, all members of the GDCh, claim till to now the online method in all seriousness to themselves.

The reason for the claim, for example, of W. Gilsbach is his statement(24. 3. 2000 letter), that he had found the phase separation of the 1985 published universal online method of Steinwandter in 1995 „**accidentally(zufällig)**". That is 10 years later than the original online method was published!

Gilsbach reported also, he was so surprised about the result of phase separation, that he repeated the online extraction procedure „**intentionally(willentlich)**".

Nobody can and could understand the claim of Gilsbach, and his claim is all the stranger as in 1993 a collaborator of W. Gilsbach participated even on a collaborative study(17, 18) **in the laboratories of H. Steinwandter**, learning all the well known advantages of the new S19® online extraction method(1-18) over the old offline methods(19-23).

As can be seen, this modern version of „**science made in germany**" of Gilsbach is only a farce(see H. Steinwandter, Counter-statement, Fresenius J Anal Chem(1996) 354: 259).

Concerning the evolution of the extraction methods it is of interest to note, that till the development of the pioneering online extraction method in 1985 all results in residue analysis obtained, for example, by the methods of Mills et al, Luke et al and Specht et al - the latter was only a derivative of the Luke et al method - were in principle erroneous.

The reason for this very kept secret situation in residue analysis was the painful fact, that the final analytical results were standardized by the estimated and therefore unknown sample water in the filtrated aqueous solvent sample extracts. Consequently the final results were also only estimates and therefore erroneous.

In 1985 this embarrassius situation in residue analysis could be eliminated by the development of the new universal S19®online extraction technique. Henceforth the online extraction technique was improved and refined continuously (1-18).

In contrast to the old offlind methods(19-23) the final analytical results of the universal S19® online extration method were standardized by the measured and therefore very well known volume of the used organic solvents(polar and nonpolar solvents).

This is reached by the pioneering new S19®online technique, by which the unknown water amount of the extracted samples was separated in one step from the organic extraction solvents, so that finally a water phase and a pure organic solvent phase was obtained. The latter volume is the sum of the used and measured polar and nonpolar solvents and consequently very well known, so that – because the results were standadized by the very well known volumes of the used and measured polar and nonpolar saolvents - for the first time exact final analytical results could be obtained.

In addition, by the new S19®online technique **all acetonitrile and acetone methods could be unified to one single universal online extraction method.**

Results

In this paper all the very pioneering results and facts of the online extraction method will be summarized.

In addition to the above milestone in calculating correct final results, other pioneering advantages of this universal online extraction technique over all offline methods are:

1. All working steps of the S19®online extraction technique are conducted in the same extraction vessel in one step,

2. In addition to the straight simultaneous and sequential working steps, any combination of both can be used,

3. no filtration step of the sample extract after the acetonitrile or acetone extraction-only used by the old offline extraction methods(19-23)-is necessary,

4. no aliquot of the sample extract after the filtration-only used by the old offline extraction methods(19-23)-is necessary,

5. no separatory funnel for the partitioning step –only used by the old offline extraction methods(19-23)-is necessary,

6. no separatory funnel for the water removal step- only used by the old offline extraction methods(19-23)-is necessary,

7. he volume of the organic phase obtained by the S19®online method is in opposition to the old offline methods(19-23)-independent of the sample water content,

8. the volume of the measured organic phase obtained by the S19®online method is- in opposition to the old offline methods(19-23)- the sum of the added volume of the polar and the nonpolar solvent,

9. the water amount of the sample extract has for the first time-in opposition to the old offline methods(19-23) –no influenceon the analytical results,

10. a minimum of extraction steps of the S19®online method results in a minimum of analytical errors,

11. a minimum of glass equipment is necessary,

12. the extraction of the S19®online method is finished after 10sec, in some cases already after 1 to 2 sec, -in opposition to the old offline extraction methods(19-23) which are finished only after 45 to 60 min,

13. instant phase separation

14. the online extraction can be represented by the Steinwandter diagrams, with water in left corner, the polar solvents(acetone and acetonitrile) in the right corner and the nonpolar solvent in the top corner of the triangles.

15. the S19®online method was tested with more than 400 pesticides and environmental chemicals with recoveries between 80 and 100%,

16. in 14 annual reports of the Hessische Landwirtschaftliche Versuchsanstalt Darmstadt the progress and development of the new one step S19®online extraction method was described in detail,

17. the S19®online extraction method was presented on several congresses and workshops.

18. the acetone and acetonitrile extraction methods could be unified to one single universal one step S19®online extraction method,

19. the universal S19®online extraction method can be – in opposition to the old conventional offline extraction methods(19-23) – miniaturized for the first time with the results, that **the solvent and chemical amounts of the S19®micro online extraction methods can be reduced to 1/10 to 1/100 of that used by the old conventional offline ectraction methods**.

These points 1 through 19 are inherent to the universal S19®online extraction method.

By this micro S19®online methods, not only is the chemical emission into the environment greatly reduced, but also the information, i.e., the benefits of analyses, is in a balanced relation to the damage caused and is therefore in harmony with the paradigma of th „Extended Categorical Imperative"(8,15).

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see also www.Steinwandter.de, Homepage, part 1.B., all contributions

5. A universal new one step micro S19®online extraction method using the binary solvent system water + acetonitrile

Zusammenfassung

Eine neue universelle einstufige S19®Mikro online Extraktionsmethode, mit dem binären Lösungsmittelsystem Wasser+Acetonitril wird beschrieben.
Die Extraktion dieser neuen S19®Mikro online Methode ist nach 10 –20 sec beendet. Diese Methode wurde mit verschiedenen Matrixproben und Pestiziden getestet. Die Wieder-findungen lagen zwischen 80 und 96%.

Summary

A new universal one step S19®micro online extraction method using the binary solvent system water+acetonitrile and NaCl as the partitioning agent is described. The extraction procedure of the universal new one step S19®online extraction technique is finished after 10

to 20 sec. The method was tested with several matrix samples and pesticides. Recoveries are between 80 and 96 %.

1. Introduction

In 1985 the universal new „Steinwandter-**19**85"one step S19®online extraction method was reported and henceforth continously improved and refined(1-18). By introduction of this new extraction technique in residue analysis all acetone and acetonitrile extraction methods(6,19-23) could be **unified to one single universal new one step S19®online extraction method** (1 – 18). This new universal one step S19®online extraction method with acetone or acetonitrile as the extraction solvents has the following pioneering and significant advantages over all old offline extraction methods.

These are:

1. All working steps of the S19®online extraction technique are conducted in the same extraction vessel in one step,

2. no filtration step of the sample extract after the acetonitrile or acetone extraction-only used by the old offline extraction methods(19-23)-is necessary,

3. no aliquot of the sample extract after the filtration-only used by the old offline extraction methods(19-23)-is necessary,

4. no separatory funnel for the partitioning step –only used by the old offline extraction methods(19-23)-is necessary,

5. no separatory funnel for the water removal step- only used by the old offline extraction methods(19-23)-is necessary,

6. the volume of the organic phase obtained by the S19®online method is in opposition to the old offline methods(19-23)-independent of the sample water content,

7. the volume of the measured organic phase obtained by the S19®online method is- in opposition to the old offline methods(19-23)- the sum of the added volume of the polar and the nonpolar solvent,

8. the water amount of the sample extract has for the first time-in opposition to the old offline methods(19-23) –no influenceon the analytical results,

9. a minimum of extraction steps of the S19®online method results in a minimum of analytical errors,

10. a minimum of glass equipment is necessary,

11. the extraction of the S19®online method is finished after 10 sec, in some cases already after 1 to 2 sec, -in opposition to the old offline extraction methods(19-23) which are finished only after 45 to 60 min,

12. instant phase separation,

13. the online extraction can be represented by the Steinwandter diagrams, with water in left corner, the polar solvents(acetone and acetonitrile) in the right corner and the nonpolar solvent in the top corner of the triangles,

14. The S19®online method was tested with more than 400 pesticides and environmental chemicals with recoveries between 80 and 100%,

15. In 14 annual reports of the Hessische Landwirtschaftliche Versuchsanstalt Darmstadt the progress and development of the new one step S19®online extraction method was described in detail,

16. The S19®online extraction method was presented on several congresses and workshops,

17. The acetone and acetonitrile extraction methods could be **unified to one single universal one stepS19®online extration method**,

18. In addition to the straight simultaneous and sequential working steps, any combination of both can be used,

19. The univeral S19®online extraction method can be – in opposition to the old convetional offline extraction mthods(19-23) – **miniaturized for the first time** with the results, that the solvent and chemical amounts of the S19®micro online extraction methods can be reduced to 1/10 to 1/100 of that used by the old convetional offline extraction methods.

Points 1 through 19 are inherent to th universal S19®online extraction method.

In the previous three papers I-III of this series(7, 9, 12) the new universal one step S19® online extraction method in the macro and micro mode using the binary and ternary solvent system with acetone as the polar solvent was described in detail.

In the presented communication the new universal one step micro S19®online extraction of samples with the binary solvent system water + acetonitrile and with NaCl as the partitionig agent is described.

2. Experimental

The preparation of representative samples, the apparatus, chemicals, solvents, gases, the determination of analytes by GC and HPLC, the priciple, illustration and description of the binary and ternary S19®online extraction methods were described elsewhere(1-18) and should not be dublicated here.

2.1. One step S19®online extraction of products with water contents greater than 70%

Weigh 10g of a homogeneous and representative fruit or vegetable subsample into a suitable extraction vessel(15), add 20ml of acetonitrile and ca 3g of NaCl. Extract with Ultra Turrax at high speed for 10 –20 sec. Centrifuge, if necessary. Pour the upper organic phase into a 25 ml Erlenmeyer flask. The extract is ready for determination by GC or HPLC(6, 17, 18, 23)

If smaller or greater sample sizes are used, reduce or increase NaCl and the solvents accordingly.

2.2. One step S19®online extraction of products with water contents lower than 15%

Weigh 0.5 - 1g of a representative subsample of e.g. 2 mm sieved animal feedstuffs or dried fruit and vegetables into a suitable extraction vessel(15), add the corresponding amount of water to reach ca a total of 10g of water and 20 ml of acetonitrile. Mix at high speed with Ultra Turrax for ca 10 –20 sec. Add ca 3g of NaCl and mix again at high speed for 10 –20 sec. Continue as described in 2.1.

If smaller or greater sample sizes are used, reduce or increase NaCl and the solvents accordingly.

2.3. Determination of the sample weight in the aliquot acetonitrile volume

The amount of sample represented in the final sample solution is calculated as follows:

$g = g_o V/V_o$, where

g = the amount of sample in the final sample extract,

g_o = the amount of sample weighed,

V = the aliquot volume of acetonitrile,

V_o = the total volume of acetonitrile.

2.4. GC and HPLC determination

a. Determination of the sample extract without cleanup

Evaporate an aliquot volume of the acetonitrile sample extract(2.1. and 2.2.) nearly to dryness. Redissolve in acetone. Repeat evaporation and make to 1 ml final volume for the determination of phosphorus pesticides by gas chromatography equipped with selective detectors e. g. FPD and NPD.

For gradient HPLC equipped with UV- and Fluorescence detectors inject the acetonitrile extract directly after water addition to obtain a 1+1 mixture and filtration through 0.22 µm filter.

b. Determination of the sample extract after cleanup

Evaporate an aliquot volume of the acetonitrile sample extract(2.1. and 2.2.) nearly to dryness and exchange acetonitrile by the appropriate solvent necessary for the following descibed individual cleanups:

a. cleanup over 10% deactivated silica gel(17, 24)
b. cleanup over celite - carcoal(20)
c. cleanup over C - 18 phases(25)

The cleaned sample extracts can now be determined by GC-ECD and all other GC and HPLC systems.

2.5. Recovery studies

a. Lettuce and pear samples(without any background residues) were subsampled and homogenized in a mixer. The lettuce and pear samples(water content greater 70%) to be analysed were then each fortified by three organophosphorus pesticides(see Table 1), homogenized, extracted(see 2.1.) and analysed by GC – FPD without cleanup.

b. Feedstuff sample(2 mm sieved and without any background residues) was fortified with two organochloro pesticides(see Table 1), homogenized, extracted(see 2.2.) and analysed by GC – ECD after cleanup over silica gel(24).

3. Results and discussion

The presented universal one step S19®online extraction technique with acetonitrile and NaCl as the extraction and partitioning agents offers various strategies to decide, what extraction sequence for what kind of samples is the most suitable:

a. analysing samples with water contents greater than 70% the extraction and partition step are conducted simultaneously in one vessel without further addition of water.

b. analysing samples with water contents lower than 15% the extraction and partition step are conducted sequentially or simultaneously in one extraction vessel, with addition of water to reach the half of the used acetonitrile volume.

For recovery discussion the added concentrations(μ/kg) of the pesticides including the mean values of four determinations, $\overline{X}(\mu$/kg), and the average recoveries(%) of the method used are listed in Table 1. For this reason, in the first column of Table1 the commodities are listed and in the second and third column the pesticides with their added concentrations. Then, in sequence, the mean values, $\overline{X}(\mu g$/kg), and the average recoveries are tabulated. From Table 1 one can see, that the average recoveries of the pesticides ranged from 80 till 96%. These results agree very well with those of the previous described micro and macro one step S19® online extraction methods using acetone as the extraction solvent(1-18).

Based on these satisfactory results, it is obvious, that the presented micro one step S19® online method can be used for routine analysis.

By this new micro one step S19®online method, not only is the chemical emission into the environment greatly reduced, but also the information, i.e.,the benefits of analyses, is in a balanced relation to the damage caused and is therefore in harmony with the paradigma of the „Extended Catergorical Imperative"(8, 15).addition of water to reach the half of the used acetonitrile volume.

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See also www.Steinwandter.de, Homepage, part 1.B., all contributions

Table 1. Recovery studies of 8 pesticides added to lettuce, pears and feedstuff samples analysed by the micro one step S19®online extraction method with acetonitrile as the extraction agent

Analysed commo-dities	Added pesticides	Added concen-trations	mean values [a] $\bar{X}$ (μg/kg) and average recoveries(%)analysed by the presented mico online extraction method	
		(μg/kg)	[a] $\bar{X}$(μg/kg)	Average Recoveries(%)
Lettuce	tolclofos-methyl	50	48	96
	parathion-ethyl	50	47	94
	methidathion	100	95	95
Pears	chlorpyrifos-metyl	40	38	95
	parathion-methyl	30	29	96
	fenitrothion	30	24	80
Feed-stuff	lindane	10	8	80
	dieldrine	30	28	93

[a]Average of four determinations

6. A 2 sec micro S19®online extraction technique for the determination of PCB´s from sewage sludge samples

Zusammenfassung

Durch die von <u>S</u>teinwandter im Jahre **19**85 entwickelten neuen bahnbrechenden universellen S19®online Extraktionsmethode ist es zum ersten Male möglich die Extraktionsgeschwindig-keiten von chemischen Verbindungen aus unterschiedlichen Matrixproben zu untersuchen. Hinsichtlich der Extraktion von PCB Kongeneren aus Klärschlämmen wurde festgestellt, daß die PCB Wiederfindungen nach 2 Sekunden zwischen 89 und 96 % lagen.
Es ist daher möglich sehr schnell festzustellen, ob eine Probe kontaminiert ist oder nicht.

Summary

By the „<u>S</u>teinwandter-**19**85" created new pioneering universal S 19®online multiresidue extraction technique it is for the first time possible to study the extraction velocities of chemical compounds from different matrix samples. Concerning the extraction of PCB congeners from sewage sludge samples it was found that the PCB recoveries are 89 - 96 % after 2 sec. Therefore one can decide very quickly if a sample is contaminated or not.

Introduction

In 1985 a considerable and significant progress and advancement was made in residue analysis by the new pioneering S19®online multiresidue extraction method(2-20), that eliminated all time consuming and costly steps like the filtration step of the acetone or acetonitrile sample extract, the aliquotation of the filtrated sample extract, the partition and shake-out steps by the use of separatory funnel,and reduced therefore all glass equippment of the old methods(21-26). In a word, this S19®online extraction method provided only one simple and therefore rapid step for the extration and partition of analytes conducted in one extration vessel, so that it is from that time on possible to decide very quickly if a sample is contaminated or not. Moreover it is for the first time also possible to study the extraction velocities of chemical compounds from various matrix samples.

A milestone of this one step S19®online extraction method however is to obtain for the first time exact analytical results, because the knowledge of the water content for the determination of the exact sample weight to be analysed is no longer necessary. Till then these necessary values, however, were not measured by the old methods(21-26), so that these errors of the water content of the sample extracts were also errors in the final spurious results. Inherent to this new S19®online extraction technique(3-20) is also for the first time an option for miniaturization, so that chemical and solvent consumtion can be reduced down to 1/10 – 1/100 of that used by the conventional old macro offline extraction methods(21-26).

In addition to these advantages it could also be shown that pesticides and environmental chemicals in feedstuffs or fruit and vegetables are extracted within 2 – 120 sec(3-20), a noticable advantage versus the longer extraction times of the old offline methods.

The necessity of these rather long extraction times for these samples is still unproven. Therefore kinetic investigations- only possible with this new one step S19®online extraction technique- were conducted by the new S19®online extraction method(3-20) to learn more about the extraction velocity of pesticides and environmental chemicals from these matrix samples into the organic phase.

In the following the extraction procedure for the fast micro S19®online isolation of PCB´s from sewage sludges is described. This paper presents first preliminary results of the new one step micro S19®online extraction of PCB´s from sewage slude samples. It was analysed that the extraction is finished after few seconds.

The cleanup over silica gel containing 10 % silver nitrate(2) and the determination of the PCB congeneres by GC-EC are described elsewhere(2) and should not be repeated here in detail.

2. Experimental

2.1. Micro S19®online extraction

Add 1g of a freeze-dried, pulverized and 0,1 mm sieved sewage sludge sample(2), 30 ml of water+acetone = 1+2, 20 ml of petroleum ether and ca 4g of NaCl into a 100ml flask. Close the flask tightly. Shake vigorously the flask by hand at ca 4 cycles/ sec for 2sec..

The over night(15h) extraction was conducted on a mechanical shaker at ca 180 cycles/min. Instant phase saparation is obtained.

The PCB´s are in the upper organic phase.

2.2. Cleanup of the sample extract

Transfer the upper organic phase(see 2.1.) into a 50 ml flask containing ca 2g of Na_2SO_4 Stir for ca 5 min. Transfer 20 ml(= 0.5g of sample) of the organic phase into a 50 ml pear-shaped flask and evaporate nearly to dryness. Add hexane and reconcentrate. Exchange hexane by petroleum ether.

Pipette the organic phase onto a glass column(i. D.) filled with 2g silca gel covered by 10% silver nitrate(2). Elute PCB isomeres with petroleum ether. Collect 80 ml of the effluent. Reduce cleaned sample extract to ca 0.5 ml. Transfer the sample extract to a 5 ml graduated tube. Fill up with hexane. The extract is now ready for GC determination.

2.3. Determination of PCB congeners by capillary GC-ECD

1 μl of the cleaned-up sample extract (see 2.2.) is injected splitless, using the fused capillary columns DB-1 and DB-5(2).

3. Results and discussion

For documentation of the capability of the new one step micro S19®online extraction two sewage sludge samples No. A and B were analysed. For that reason the PCB concentrations(μg/kg) and the average recoveries(%)of the six congeners(PCB-IUPAC-No.: 28, 52, 101, 138, 153 and 180) of the 2 sec and 15h extraction were analysed and shown in Table 1.

In the first column of Table 1 the sewage sludge samples No. A and B are listed and in the second and third the extraction times and the PCB concentrations(μg/kg) of the PCB-IUPAC-No.:28, 52, 101, 138, 153 and 180 obtained after the extraction times of 2 sec and 15h. In the brackets the PCB recoveries(%) compared with the values of the 15h micro S19®online extraction can be seen. One can see from Table 1, that the PCB recoveries are between 89-96% compared with the 15h extraction values taking these as 100%. It should be also mentioned, that the 15h extraction values of the micro S19®online method are till a factor 2-3 higher(1) than the values obtained by the official soxhlet extraction method of the German Government(2), an indication of quantitative working of the S19®micro online method. According to these satisfactory results, it is obvious, that the presented micro S19®online method can be used for PCB extraction from sewage sludge samles in routine analysis.

It shoud be also noted, that these extraction studies could be only conducted by the new extraction technique of the presented S19®online extraction method.

The advantages of this new one step universal S19®online extraction technique compared with all other old offline extraction methods(21-26) are:

1. all working steps of the S19®online extraction technique are conducted in the same extraction vessel in one step,

2. in addition to the straight simultaneous and sequential working steps, any combination of both can be used,

3. no filtration step of the sample extract after the acetonitrile or acetone extraction-only used by the old offline extraction methods(21-26)-is necessary,

4. no aliquot of the sample extract after the filtration-only used by the old offline extraction methods(21-26)-is necessary,

5. no separatory funnel for the partitioning step –only used by the old offline extraction methods(21-26)-is necessary,

6. no separatory funnel for the water removal step- only used by the old offline extraction methods(21-26)-is necessary,

7. the volume of the organic phase obtained by the S19®online method is in opposition to the old offline methods(21-26)-independent of the sample water content,

8. the volume of the measured organic phase obtained by the S19®online method is- in opposition to the old offline methods(21-26)- the sum of the added volume of the polar and the nonpolar solvent,

9. the water amount of the sample extract has for the first time-in opposition to the old offline methods(21-26) –no influence on the analytical results,

10. a minimum of extraction steps of the S19®online method results in a minimum o analytical errors,

11. a minimum of glass equipment is necessary,

12. the extraction of the S19®online method is finished after 10sec, in some cases already after 1 to 2 sec, -in opposition to the old offline extraction methods(21-26) which are finished only after 45 to 60 min,

13. instant phase separation,

14. the online extraction can be represented by the Steinwandter diagrams, with water in left corner, the polar solvents(acetone and acetonitrile) in the right corner and the nonpolar solvent in the top corner of the triangles,

15. the S19®online method was tested with more than 400 pesticides and environmental

chemicals with recoveries between 80 and 100%,

16. in 14 annual reports of the Hessische Landwirtschaftliche Versuchsanstalt Darmstadt the progress and development of the new one step S19®online extraction method was described in detail,

17. the S19®online extraction method was presented on several congresses and workshops.

18. the acetone and acetonitrile extraction methods could be unified to one single universal one step S19®online extraction method,
    and

19 the universal S19®online extraction method can be – in opposition to the old conventional offline extraction methods(21-26) – miniaturized for the first time with the results, that **the solvent and chemical amounts of the S19®micro online extraction methods can be reduced to 1/10 to 1/100 of that used by the old conventional offline ectraction methods**.

These points 1 through 19 are inherent to the universal S19®online extraction method.

By this micro S19®online methods, not only is the chemical emission into the environment greatly reduced, but also the information, i.e., the benefits of analyses, is in a balanced relation to the damage caused and is therefore in harmony with the paradigma of th „Extended Categorical Imperative"(10,17).

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See also www.Steinwandter.de, Homepage, part 1. B., all contributions

Table 1   Results of PCB extraction from two sewade sludge samples analysed by the micro
S19®online multiresidue method

Sewage sludge sample No.	Extraction time	Mean values [a] $\bar{X}$(μg/kg) and average recoveries[b](%) of PCB congeners					
		No. 28	No.52	No.101	No.138	No.153	No.180
A	2 sec	244[b](92)[d]	140(91)	184(96)	272(94)	257(89)	157(92)
	15h	266[c](100)	154(100)	192(100)	290(100)	288(100)	170(100)
B	2 sec	379(92)	207(91)	157(91)	182(89)	180(91)	112(95)
	15h	409(100)	227(100)	172(100)	204(100)	197(100)	118(100)

[a]Average of four determinations;

[b]Average recoveries(μg/kg) of the 2 sec extraction compared with the 15h extraction;

[c]Average recoveries(μg/kg) of the 15h extraction taken as 100%:

[d]Average recoveries in % of the 2 sec extraction compared with the 15h extraction taken as 100%.

7. Kinetics of PCB extraction from sewage sludges using the ternary solvent system <u>water-acetone-petroleum ether</u>

Summary

The extraction rates of six PCB congeners of two freeze-dried sewage sludge samples were studied by the universal micro S19® online extraction method in the simultaneous mode using the ternary solvent system <u>water-acetone-petroleum ether</u>. It was found, that the PCB`s were extracted from the samples by a fast and slow extraction step.
The extraction rates were discussed in terms of their half times, which were calculated by the slopes of the corresponding regression lines. The mean values of the half times of the fast extraction step are between 0,5 and 0,8 sec and those of the slow extraction step are between 24 and 27 sec.

1. Introduction

In part 6 of this series the results of the PCB extraction from two sewage sludge samples were reported. It was shown that the extraction was finished after 2 sec with recoveries of about 90%.
In this paper the PCB extraction rate in dependence of the extraction time will be discussed using the ternary solvent system <u>water-acetone-petroleum ether</u> of the pioneering universal micro S19®online extraction method(1-18).

2. Experimental

2.1. Sample preparation

For kinetic investigations of the PCB extraction the two sewage sludge samples A and B of the 1992 Umweltbundesamt(UBA) collaborative study were analysed.

2.2. Extraction of PCB`s

Weigh 1g of samp into a 100 ml flask. Add 30 ml of water +acetone = 1+2, 20 ml of petroleum ether and ca 4g of NaCl. Close the flask tightly. Shake the flask for 2 sec; 5 sec; 15 sec; 30 sec and 15h.

After extraction transfer the organic phase into a 50 ml Erlenmeyer flask containing ca 2g of Na_2SO_4. Transfer 20 ml of the dried sample extract into a 50 ml pear-shaped flask and evaporate to ca 0,5 ml. Repeat evaporation twice to ensure the complete removal of acetone. The extract is now ready for cleanup

2.3.Cleanup of sample extract

Fill 2g of silica gel containing 10% silver nitrate(w/w) into a glass column(i.D. = 7 mm). Pipette the sample extract obtained in 2.2. onto the column. Elute the PCB`s with petroleum ether. Collect 80 ml of the effluent. Reduce volumn and transfer the sample to a 5 ml graduated tube.

The extract is now ready for capillary GC-determination.

2.4.GC-ECD determination of PCB`s

Inject splitless 1µl of samle extract of 2.3. using the fused capillary columns DB-1 and DB-5.

3. Results and discussion

The distribution of PCB`s into a two phase system, e.g. into an aqueous and a organic phase, is a pseudo-unimolecular reaction.

If **a** is the initial PCB concentration and **x** is the concentration of PCB`s in the organic phase after extraction time **t** the PCB`s remaining in the aqueous phase will be (**a-x**).

Thus the disappearance of PCB`s from the aqueous phase, which is equal to the rate of the PCB extraction into the organic phase, is

-d(a-x)/dt = k(a-x)   or   **dx/dt = k(a-x)**

from where with **x** = 0 at **t** = 0

log(a-x) = log**a**-0,4343**kt** is obtained,

so that from the slope of the line the velocity constant **k** can be evaluated. Therefore, the greater the velocity constant **k** of the PCB extraction, the faster the PCB extraction rate, the greater is the slope of the corresponding line.

The half time $t_{1/2}$ of the PCB extraction, which is the time after which the PCB conentration in the aqueous phase is reduced, i. e., **x** is equal **a/2**, is therefore

$t_{1/2}$ = 0,6931/**k**

The **k** and $t_{1/2}$ values of the PCB extraction rates were calculated in this study by the slopes of the corresponding regression lines, which are known as the straight lines lying closest to all measured points on the scatter plot.

Because two processes with different extraction rates are acting in the PCB extraction system, as can be seen in Fig.1 and Fig.2, a curve is measured which is composed by the two straight lines of different slopes. Therefore we obtain two half times, one for the fast and one for the slow extraction rate.

This is shown in Fig.1 and Fig.2, when the unextracted PCB concentrations **(a-x)** of the six PCB`s of the samples A and B are plotted against the extraction times. One can see, that the extraction rate is determined by the above two mentioned processes. Therefore a curve with finally two lines is obtained, whereby the slopes of their regression lines are direct related to the two extraction rates.

We can also see in Fig.1 and Fig.2, that the slopes of the regression lines of the six PCB`s are very similiar, so that the extraction rates and the half times of each PCB congener are also very similiar. Therefore the corresponding values were averaged to obtain the the mean values of the half times $\overline{t}_{1/2(f)}$ and $\overline{t}_{1/2(s)}$ for the _f_ast and _s_low extraction rate.

The half times of the PCB extraction of the samples A and B are 0,57 sec and 0,52 sec for the fast extraction process $\overline{t}_{1/2(f)}$, and 24 sec and 27 sec for the half times of the slow extraction rates $\overline{t}_{½(s)}$.

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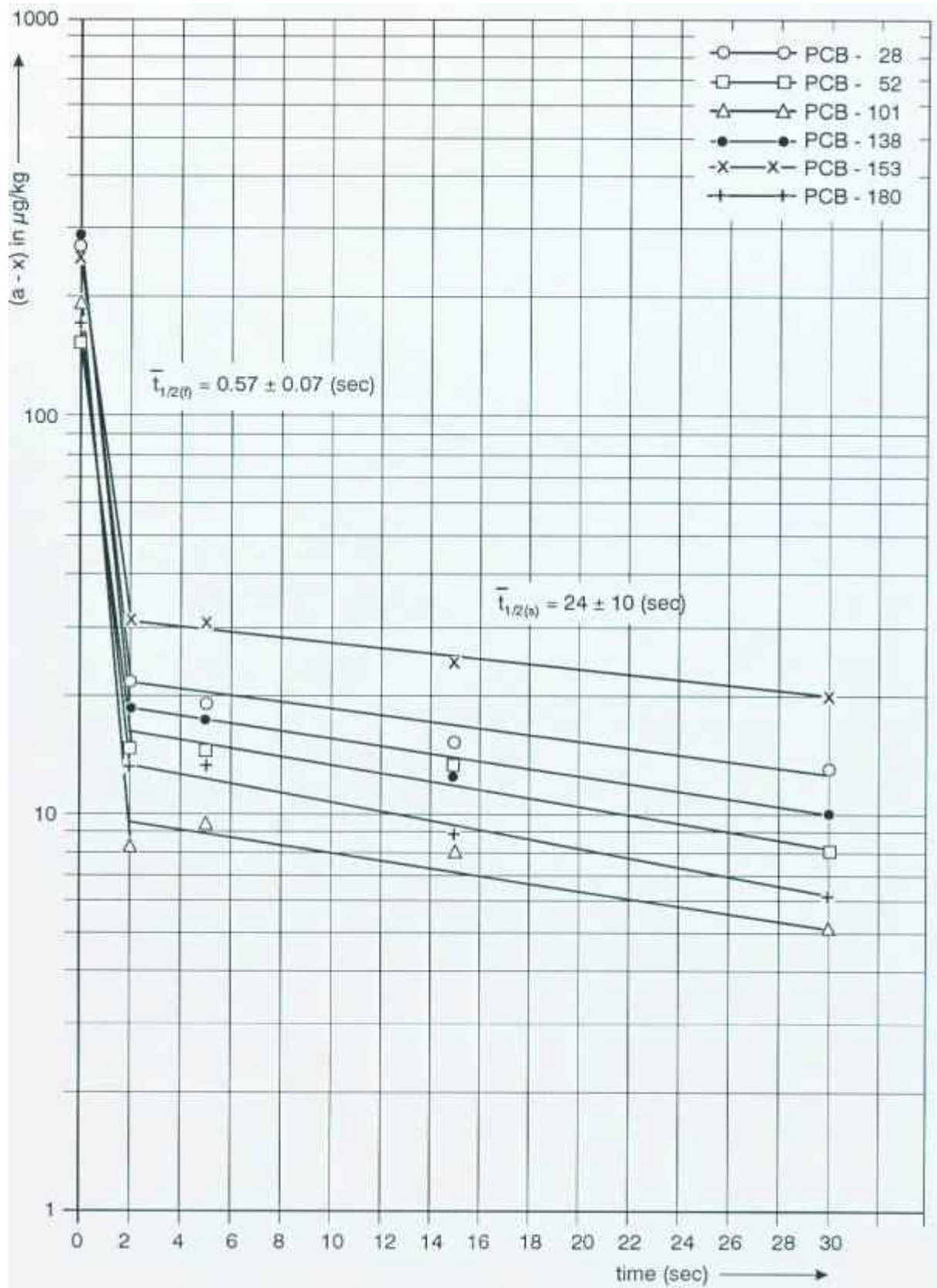See also www.Steinwandter.de, Homepage, 1. B., all contributions

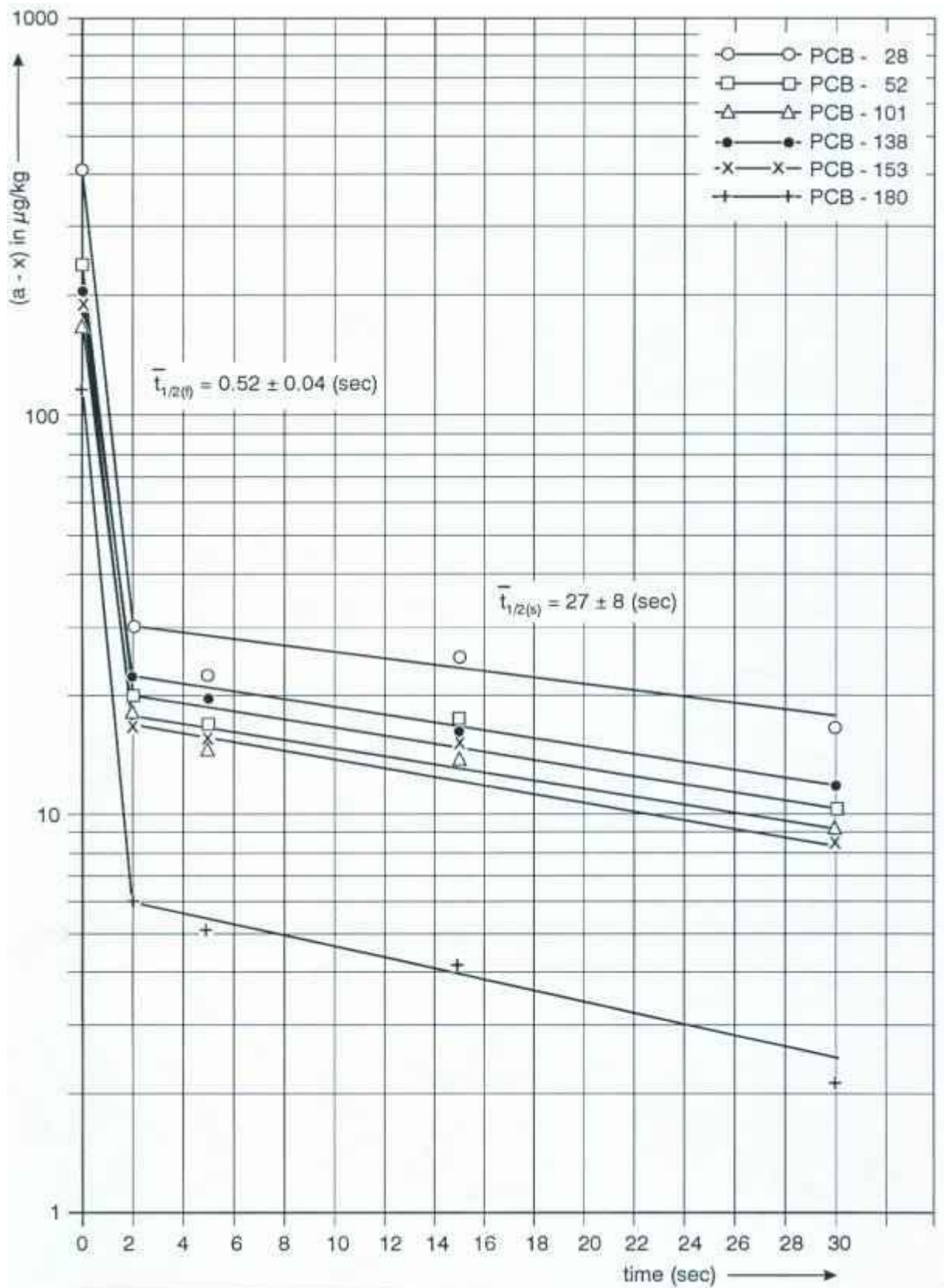**Figure 1.** Kinetics of PCB extraction from sewage sludge sample A

Figure 2. Kinetics of PCB extraction from sewage sludge sample B

8. Kinetics of PCB extraction from sewage sludges using the binary solvent system <u>water-acetone</u>

Summary

The extraction of six PCB congeners of two freeze-dried sewage sludge samples were studied by the universal **<u>micro</u>** S 19®online extraction method in the simultaneous mode using the **binary** solvent system **<u>water-acetone.</u>** It was found, that the PCB´s were also extracted from the samples by a fast and slow extraction step, as in the ternary solvent system descibed in contribution No.7.

The extraction rates were discussed in terms of their half times. The mean value of the half time of the fast extraction step was 0,68 sec and 26 sec for the slow extraction step. Analysing a pure PCB standard solution only the fast extraction step was measured with a value of 0,74 sec. This investigations were only possible by using the pioneering S 19®online extraction method.

By the use of this pioneering **<u>micro</u>** S19®online extraction method not only is the chemical emission into the environment greatly reduced, but also the information, i. e., the benefits of analyses, is in balanced relation to the damage caused and is therefore in harmony with the paradigma of the "Extended Categorical Imperativ"(8,15).

1.Introduction

In part 6 and 7 of this series the result of the PCB extraction from two sewage sludge samples with the terary solvent system water-acetone –petroleum ether were reported.

In this paper the PCB extraction rate will be discussed using the **binary** solvent system **<u>water-acetone</u>** of the pioneering universal micro S19®online extraction method of H. Steinwandter(1-18).

2. Experimental

2.1. Sample preparation

For kinetic investigations the sawage sludge sample A of the 1992 Umweltbundesamt(UBA) collaborative study and a pure solvent solution of six PCB congeners were analysed. The sample was freeze-dried and pulverized. Finally the sample was sieved to ca. 0.1 mm.

2.2. Kinetics of PCB extraction of sample A

Weigh 1g of sample into a 100ml flask. Add 30 ml of water+acetone and ca 4g of NaCl. Close the flask tightly. Shake 2 sec, 5 sec and 15 sec. The overnight extraction(15h) was conducted on a mechanical shaker. Transfer 9 ml(= o.9g of sample) into a 50 ml Erlenmeyer flask containing ca 2g of Na_2SO_4. Add ca 20 ml of petroleum ether. Stopper the flaskand gry the extract. Transferthe organicphaseinto a 50 ml pear-shaped flask and evaporate under reduced pressure to a volume of ca 0.5 ml. Repeat evaporation twice to ensure the complete removal of acetone. This extract is now ready for clean-up descibed in chapter 2.3.

2.3. Cleanup of sample extract

Fill 2g of silica gel containing 10 % silver nitrate(w/w) into a glass column(i.D.=7mm). Pipette the sample extract obtained in 2.2. onto the column. Elute the PCB`s with petroleum ether. Collect 80 ml of the effluent. Reduce volume and transfer the sample to a 5 ml graduated tube. The extract is now ready for capillary GC-determination.

2.4. GC-ECD determination of PCB`s

Inject splitless 1 µl of sample extract of 2.3. using the fused capillary columns DB-1 and DB-5.

3. Results and discussion

As discussed in part 7 of this series the distribution of PCB`s into an aqueous and an organic phase is a pseudo- unimolecular reaction.

Thus the disappearance of PCB`s fom the aqueous phase, which is equal to the rate of the PCB extraction into the organic phase, is

$-d(a-x)/dt = k(a-x)$ or $dx/dt = k(a-x)$

from where with $x = 0$ at $t = 0$

$\log(a-x) = \log a - 0{,}4343kt$ is obtained,

so that from the slope of the line the velocity constant **k** can be evaluated. Therefore, the greater the velocity constant **k** of the PCB extraction, the faster the PCB extraction rate, the greater is the slope of the corresponding line.

The halfe time $t_{1/2}$ of the PCB extraction, which is the time after which the PCB concentration in the aqueous phase is reduced, i. e., x is equal a/2, is therefore

$t_{1/2} = 0{,}6931/k$

The **k** and $t_{1/2}$ values of the PCB extraction rates were calculated in this study by the slopes of the corresponding regression lines, which are known as the straight lines lying closest to all measured points on the scatter plot.

In Fig. 1 and Fig. 2 the unextractd PCB concentrations (a-x) of the six PCB congeners of sample A and those of a pure PCB solvent system are plotted against the extraction times t. Because two processes with different extraction rates are acting in the PCB extraction system, as can be seen in Fig. 1, a curve is measured which is composed by the two straight lines of different slopes. Therefore we obtain two half times, one for the fast and one for the slow extraction rate.

Because the slopes of the regression lines of the six PCB`s are very similar, it follows, that the extraction rates and the half times of each PCB congener are also very similar. Therefore the corresponding values were averaged to obtain the mean values of the half times $\overline{t}_{1/2(f)}$ and

$\overline{t}_{1/2(s)}$ for the *f*ast and the *s*low extraction rate. The half times of the PCB extraction of sample A are 0.68 sec for the fast extraction process and 26 sec for the slow process. However, in contrast to the sample extraction shown in Fig 1, the PCB extraction rate of the pure binary solvent system, see Fig.2, is determined only by the above mentioned **fast**

process, so that in this case only a straight regression line is observed. The mean value of the half time for the fast extraction process is 0,74 sec.

Compared with the half time of ca 0,55 sec of the ternary solvent system(see contribution 7) the half time of the binary solvent system is by a factor of ca 1.25 greater.

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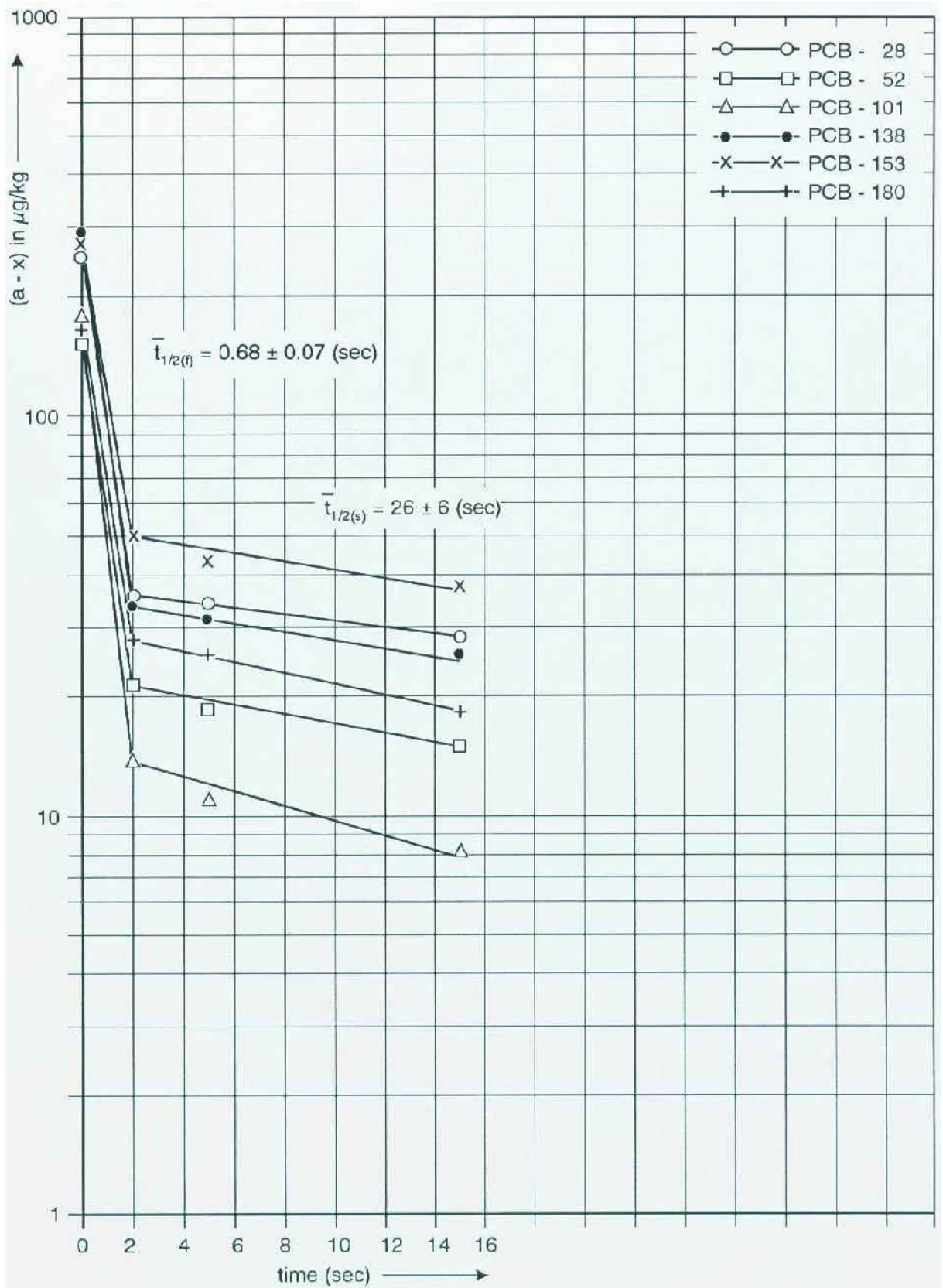See also www.Steinwandter.de, Homepage, part 1. B., all contributions

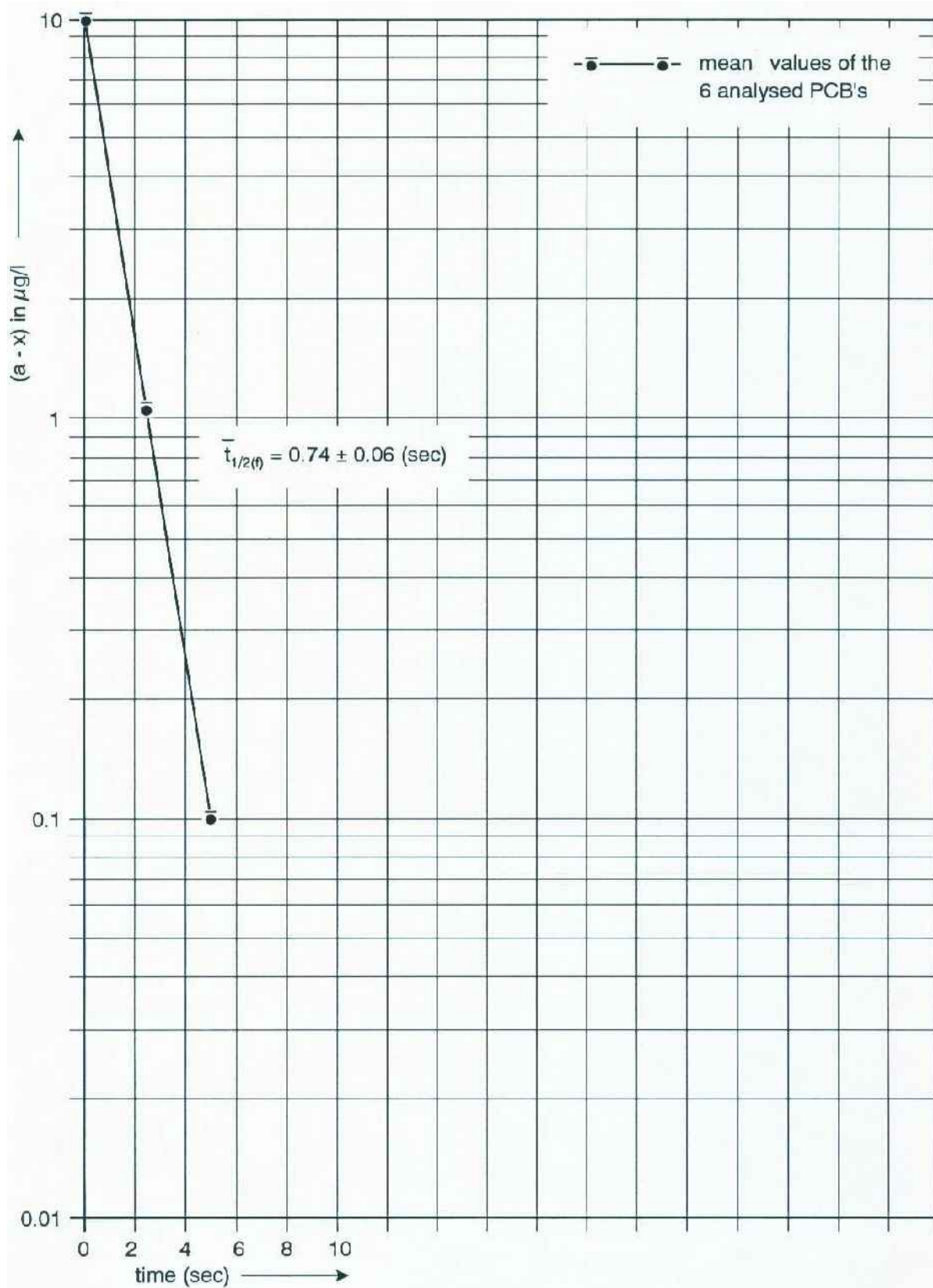**Figure 1.** Kinetics of PCB extraction from sewage sludge sample A

Figure 2. Kinetics of PCB extraction from pure binary solvent system