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MODERN ATOMIC ABSORPTION SPECTROMETRY: ACHIEVEMENTS AND FUTURE PROSPECTS

Modern trends in development of various branches of atomic absorption spectrometry (AAS) are discussed. Most important direction seems to be further development of multi-element AAS and its wider introduction into practice. Widespread of hydride generation AAS to the elements that does not form volatile hydrides (such as Rh, Mn, Cd, etc.) is of interest from viewpoint of development of extremely sensitive methods of analysis and of general chemistry. Although basics of electrothermal AAS are mostly formulated as well, further works in chemical modifiers and development of the methods of direct analysis of solids are still actually. Very important point of activity of specialists in AAS is wider application of their achievements in the practice of service laboratories, via wider introduction of the corresponding methods to international and national standards.

Atomic absorption spectrometry (AAS) has a long history (for references, see [1]). Its first analytical application was devoted to the determination of mercury by cold vapour technique as early as in 1939 [2]. However, real ascent of AAS started with appearance of flame atomization AAS (FAAS) invented by Sir Alan Walsh in 1956 [3]. Three years later Boris L'vov made a significant development of the method introducing atomic absorption spectrometry with the graphite atomizer [4], nowadays is usually called electrothermal atomic absorption spectrometry (ETAAS). The third principal development of the method was introduction of hydride generation technique (HG-AAS) in 1969 by Holak [5]. Nowadays one may definitely say that all these four branches of AAS successfully withstood the test of time.

In 1989, Hieftje [6] on the basis of function of the number of publications devoted to AAS on the year of their publication predicted that already in 1997 no further articles in this field will be published. These calculations were critically discussed by L'vov and Slavin [7]. They correctly indicated that FAAS and ETAAS (most widely used branches of AAS) have been developed independently. Therefore, the number of the corres-

ponding publications has to be analyzed separately. That is why prognosis of Hieftje was not realized, at least, on the quantitative level. Although the number of the articles on AAS published every year permanently shrinks, several directions of research are still actually. In spite of this, one may assume that the epoch of the fundamental developments in AAS is finished.

Actual directions of research for general AAS

AAS became very widespread method of analysis due to its high sensitivity, relative simplicity, high speed and rather cheap equipment. Main disadvantage of the method is its mono-element character (e.g., [6]). This disadvantage became even more important when powerful multi-element techniques, such as ICP-AES and ICP-MS, became available.

About 15 years ago AA spectrometers from Instrumentation Laboratory (USA) and Hitachi (Japan) that allow the simultaneous determination of several analytes appeared on the market. The same feature is characterized more recent AA spectrometers from Perkin-Elmer (USA), models SIMAA 6000 and SIMAA 6100. The principal scheme of all these devices is based on convergence of the beams from several light sources (hollow

cathode lamps or electrodeless discharge lamps) in one beam before the atomizer, and registration of the light intensity after monochromator at several wavelengths. However, the maximum number of simultaneously determined analytes using this equipment did not enhance 6. This may be enough for solution of some tasks, but for solution of most environmental problems these possibilities of the method are definitely insufficient. Moreover, the detection limits in multi-element regime were worse compared those for one-element determinations.

In the 1990s, the specialists headed by Becker-Ross [8, 9] from the Institute for Analytical Sciences (Berlin) have developed really multi-element AA spectrometer (HR-CS AAS) that uses continuous spectrum of a xenon short arc lamp as a light source. I ought to mention that analogous works were conducted already in 70th (e.g., [10]). However, the detection limits reached were significantly worse compared to those reached with the sources of linear radiation. Re-vitalization of the idea became possible after significant development in the corresponding hardware. The authors [8, 9] assert that the detection limits reached with HR-CS AAS are close to those of modern single-element devices.

The other advantage of the new device is its unique background correction ability. As is known, the systems of background correction actually used possess some disadvantages. Deuterium correction is not effective towards the structured background, and application of Zeeman background correction results to about 30 % decrease in sensitivity. Application of a continuous light source in a tandem with high-resolution monochromator allows conducting the correction very near to the resonance line of the analyte used, but without any losses in sensitivity. The impressive example of practical application of this system may be found in [11]. Using HR-CS AAS, Welz et al. could directly determine thallium in suspensions of marine sediment reference materials without chemical modifiers (pure thallium solutions were used for construction of the calibration graph). Clear analytical signal of thallium was obtained after subtraction of spectrum of main interferent (SO_2) from the total signal measured. Recently the authors of new spectrometer published a monograph completely devoted to description of its construction and possibilities [12].

Application of diode lasers is one more promising direction of development of AAS possessing

a long history. Diode lasers were proposed to be used as light sources instead of hollow cathode lamps in 1988 [13]. As diode lasers are characterized with high intensity and extremely low noise, their application lowers the detection limits 10-1000-fold depending on the analyte. The high spectral purity of a diode laser in single-mode operation dramatically simplifies the spectral isolation of the absorption signal. Therefore, there is no need for a monochromator in this case. Then, very narrow spectral lines of the diode laser enables isotope selective analysis for light and heavy elements, such as Li and Pb or U, respectively, which show relatively large isotope line shifts. Finally, modern diode lasers are cheap and reliable. That is why they seem to be quite prospective for wider introduction in analytical practice [14].

From formal viewpoint, one more permanently developed direction of AAS is its application in speciation studies. However, in this case AAS is used only as detector, and main efforts are concentrated on the development of the reliable separation techniques. Therefore, numerous works of such a type contribute quite little to development of AAS itself.

Actual directions of research for HG-AAS

As is known, HG-AAS was proposed mainly for improvement of the determination of Se and As (sensitivity of their determination by FAAS is quite low). HG-AAS is a typical hybrid method of analysis [15] where pre-concentration of an analyte is an integral part of its subsequent determination procedure. The method possesses numerous advantages, first of all separation of analytes forming volatile hydrides (mostly semi-metals) from the matrix. Simultaneously absolute sensitivity of the method is significantly increased as rather large sample volume (up to 50 ml) may be used for formation of the single analytical peak. Method is easily automatized using commercial equipment, that is why it is quite widespread. Peculiarities of the method are discussed in detail in comprehensive monograph [16].

However, significant disadvantage of HG-AAS is rather pronounced matrix interferences. They are caused by the influence of the sample matrices on the processes of formation of volatile hydrides and by gas-phase interferences in low-temperature quartz atomizers [16]. Then, wide introduction of platinum metals as chemical modifiers especially effective towards semi-metals made their determination in complex samples by ETAAS a routine procedure. That is why namely ETAAS

is often a method of choice nowadays for the determination of hydride forming analytes in complex matrices.

Further development of HG-AAS is mostly related to the works headed by Ralph Sturgeon [17]. In 1995, Sanz-Medel et al. [18] observed volatilization of cadmium during execution of the standard HG-AAS determination procedure. However, according to modern chemistry cadmium does not form volatile hydrides. Later analogous data were obtained for Cu, Au, Ag, Zn, Rh, Pd, In, Tl, Co, Cr, Fe, Os, Ru, Mn and Ni (for references, see [17]). Till now nature of the volatilized species is not completely clear. One hypothesize that sodium borohydride reduces analyte compounds to tiny particles of elemental analytes. In pure solutions, the generation efficiency for the analytes listed above is in the range of 8–90 % depending on the experimental conditions [17]. Although nowadays this approach is not competitive with ETAAS for solution of common tasks, it may be very prospective for analysis of extremely diluted solutions. In this case low recovery of the analytes will be compensated by the possibility of their effective pre-concentration with low values for blank experiments.

One more prospective direction of research in HG-AAS is generation of hydrides by electrochemical reduction, not by using chemical reagents [19, 20]. Main attraction of this approach is avoiding of addition of large amounts of the reductants thus lowering significantly the detection limits. Taking into account that main field of application of HG-AAS shifts to its use for the determination of ultra-traces of analytes, this is a quite promising approach.

Actual directions of research for ETAAS

ETAAS has two main steps in its development, namely before and after introduction of the STPF concept proposed by Slavin et al. [21] in 1981. High sensitivity reached using relatively cheap equipment always was a key advantage of the method. However, euphoria of the first publications was substituted rather fast with scepticism towards perspectives of ETAAS because of pronounced matrix interferences. Wide introduction of the STPF concept into analytical practice resulted to creation of "interference-free" ETAAS. Although this definition is not quite correct, this concept was a great step ahead in the development of the method.

For better understanding of further reasoning, the key positions of the STPF concept have to be

reminded. These are [21]: evaporation of samples from graphite platform; registration of peak areas; "gas-stop" mode at the atomization stage; application of a pyrolytic graphite for graphite atomizers; Zeeman background correction; fast electronics; application of chemical modifiers.

Nowadays qualified usage of modern equipment "automatically" solves many problems preventing successful determinations by ETAAS 20 years ago. However, successful solution of many analytical tasks needs the adequate chemical modifier to be chosen as well. This 7th point of the concept cannot be realized in the construction of the ETAAS equipment and must be chosen by the analyst. That is why nowadays development of ETAAS is mostly connected with perfection of our knowledge concerning most effective application of chemical modifiers.

Chemical modifiers. Reagents added into the electrothermal atomizer for improvement of selectivity of the method have been used in ETAAS since 1971 [22]. In 1973, Ediger [23] systematized this approach and formulated the concept of. Later on it became a component part of the STPF concept. Intensive investigations of chemical modifiers resulted to invention of very effective modifiers mostly belonging to one of the following groups [24]: nitric and oxalic acid and their ammonium salts; metal nitrates (except platinum metals); ammonium phosphates; refractory carbides (WC, ZrC, MoC, etc.); organic compounds (mostly ascorbic and citric acids and their salts); *d*-elements in high oxidation states (WO_4^{2-} , VO_3^- , etc.); platinum metals (PMs), except Os.

Effectiveness of correctly chosen chemical modifiers is very high. For example, application of oxalic acid allows conducting direct determination of Cd and Pb in sea water [25, 26]. The most actual problem nowadays is not invention of new modifiers, but formulation of clear rules for optimum application of well-known ones. Evidently that one-by-one comparison of chemical modifiers is a time-consuming procedure without any guarantee in its happy final. Very attractive is a choice of optimum modifier made on a paper, on the basis of understanding of probable interactions among modifier, analytes and sample matrix. That is why many efforts have been spent for researches of the corresponding mechanisms.

Sometimes such mechanisms are relatively simple, and the corresponding investigations only support the quite evident interactions. For example, this is true towards formation of refrac-

tory analyte phosphates in the presence of ammonium phosphates as the modifiers [27] or volatilization of chloride-ion from inorganic chlorides in the presence of nitric acid [28]. However, mechanisms of the action of platinum metal modifiers are still under discussion [29, 30]. In addition to complexity of the problem (one has to analyze numerous interactions in the system Analyte—Modifier—Matrix—Graphite in the temperature range 20—2500 °C and to find out reactions that exert the decisive influence over on the effectiveness of the modifier), there are some difficulties of a methodological nature as well [31].

Most important that modern methods of research often do not allow receiving a simple answer to the nature of interactions between ng-amounts of substances. Methods of monitoring of chemical transformations in systems like these during their heating (mostly various X-ray techniques) are of relatively low sensitivity. However, interactions between clusters of substances may differ significantly from those between their bulk amounts. The data of indirect methods of research (determination of activation energy of the corresponding processes, mass-spectrometric analysis of the gaseous phase or radiotracer technique) may be interpreted in a different way.

Therefore, a problem of criteria of correctness of mechanisms developed is of great importance. In the absence of a possibility to obtain a simple answer, originality of the mechanisms proposed is often evaluated as criterion of their scientific value. However, the best criterion of correctness of the mechanisms of action of the modifiers proposed is important improvement in their practical applications reached as a result of theoretical researches. Alas, usually theoretical researches of chemical modifiers do not have a deal with their practical applications, and this criterion is simply ignored.

For example, in the first works devoted to investigations of the action of PM modifiers main attention was paid to processes taking place during the atomization stage (e.g., [32]). No new modifiers or any improvements for existing ones were proposed on the basis of the concepts developed. Analysis of the problem proved that effectiveness of PM modifiers is mostly determined by the processes taking place during the pyrolysis stage [33]. This approach proved to be rather fruitful. It allowed to create step-by-step scheme of interactions in the graphite atomizers in the presence of PM modifiers [34] and to propose

some new forms of them, namely complex ammonium oxalatopaladate $(\text{NH}_4)_2[\text{Pd}(\text{C}_2\text{O}_4)_2]$ and colloidal palladium [35].

The point is that definite active form of PM modifiers is elemental metal (probably, the corresponding oxides possess the modifying properties as well). The lower temperature of formation of elemental PM in the atomizer, the higher efficiency of the modifier is reached. Under carefully optimized conditions, efficiencies of colloidal Pd and other Pd modifiers are similar [35]. However, the former modifier is very robust and does not need this careful optimization; when, it is not susceptible to the negative influence of the sample matrices [36].

Nowadays, huge amount of the experimental data collected and numerous theoretical investigations create a solid basis for the possibility to choose optimum modifier "in advance", on the basis of the data on the nature of analytes and sample matrices. The problem is that the number of researchers who may operate with these data is rather small. Most researchers have to waste a lot of time trying to apply the modifiers that are definitely not effective for analysis of given samples.

Quite disappointing is that nowadays the data obtained during the simplest optimization of the determination conditions in the presence of different modifiers are often used for speculations on mechanisms of their action. That is why the level of modern works in this field is usually lower compared to those made a decade ago. This situation looks illogical, but it has a quite realistic basis. Many brilliant researchers who made their names with deep laborious researches in ETAAS either finished their scientific career (such as W. Slavin or D.L. Styris) or shifted their research interests to other fields of science (B.V. L'vov to kinetics, W. Frech to speciation of mercury traces, R. Sturgeon to ICP-MS and HG-AAS, J.A. Holcombe to ICP-MS). Then, nowadays ETAAS is often evaluated as well-developed and not prospective direction of researches from viewpoint of scientific career (and receiving the research grants, too). That is why many investigations in ETAAS are conducted by young researchers from developing countries who are not qualified enough for real development of the method.

New atomizers. The possibilities of modern side-heated graphite furnaces with integrated platforms significantly exceed those of earlier end-heated atomizers. However, efforts to invent new more progressive constructions are still popular. Main efforts are concentrated on 2-step atomizers.

This concept is not new. In practice, L'vov cuvette [4] was the first atomizer of such a type. Possibility to govern independently by processes of vaporization and atomization of the sample significantly broadens of the analyst ability to analyze complex samples. More than 15 years ago Frech et al. [37] created very successful construction of 2-step atomizer. Using this atomizer, they could analyze directly most samples using pure standard solutions for calibration purposes. However, this could not be done "automatically". Optimization of the determination conditions was a tedious procedure that needed deep understanding of the nature of the processes taking place in the atomizer [38]. Therefore, the atomizer may be used effectively only by the qualified analysts. This was one of the reasons why the 2-step atomizer by Frech did not become widespread (its second disadvantage was relatively high price). The actual serial atomizers suit quite well to the contradictory demands of high efficiency, relative simplicity and moderate price.

The recent achievements in the same direction belong to Nagulin et al. [39]. They proposed a remake of the standard graphite atomizer that transforms it to a 2-step atomizer. Relative simplicity of the construction is a definite advantage of the new device. However, high demands to qualification of the analyst are kept that may possess negative influence on the future of the atomizer.

Direct analysis of solid samples. As indicated above, the STPF concept solved the problem of low selectivity of early ETAAS. The solution was so effective that modern ETAAS belongs to few methods suitable for direct analysis of solids [40]. This approach possesses numerous advantages, such as sharp decrease in analysis time, elimination of analytes losses and contamination of samples during their decomposition, significant decrease in the determination limits, etc. No wonder, that history of direct analysis of solids by ETAAS exceeds 30 years (e.g., [41]). Nevertheless, this approach is still quite exotic. This is caused by its disadvantages that are quite pronounced as well. These are more severe matrix interferences, problems with adequate calibration, high demands to homogeneity of samples and necessity to apply AA equipment suitable for operations with solid samples.

First two problems are similar to those known for analysis of solutions and often may be solved by careful optimization of the determination conditions. Situation with homogeneity of samples

is more specific and significant, especially taking into account that only about 1 mg of sample is used for one measurement. That is why reaching high homogeneity of originally very inhomogeneous natural samples turns up a serious problem. However, this problem is less pronounced for synthetic materials, such as high purity materials [42] and pharmaceuticals [43]. Therefore, direct determination of impurities in these materials by ETAAS is especially prospective. As for the determination of metal traces in plastics, it looks like nowadays their direct analysis by ETAAS is one of the fastest, simplest and most effective methods for solution of this task (e.g., [44]).

The last not the least drawback of direct analysis of solids by ETAAS is impossibility to conduct them using most of modern AA equipment. The only firm that fills this niche up is Analytik Jena (Germany). It produces an electrothermal atomizer suitable for direct analysis of solids and an autosampler, which allows providing analysis in automatic regime [45]. The general level of this equipment is high that makes prospects in development of direct analysis of solids by ETAAS quite firm.

Actual directions of research for FAAS and mercury cold vapor method

Development of FAAS and mercury cold vapor method seems to be mostly finished. In spite of this, many application articles are still published every year. Usually they describe slight improvements of well-known approaches to analysis (for references, see [46]). In FAAS this mostly concerns its coupling with various flow injection pre-concentration methods. As for cold vapor technique, this is application of exotic sorbents (such as Au-treated carbonized nut shell) for pre-concentration of mercury vapors.

Wider introduction of AAS to routine analyses

In addition to the actual directions of researches in modern AAS listed above, one more important task is wider application of AAS in service laboratories. First of all this concerns ETAAS, as FAAS is already used there rather intensively. The best way for evaluation of widespread of analytical method for routine analysis is evaluation of extent to which it has spread in the corresponding standard methods of analysis (international ASTM and ISO, Russian GOST, etc.). The total number of the methods having deal with "electrothermal AAS" or "graphite fur-

nace AAS" found on the official ASTM page (<http://www.astm.org>) is 33. The corresponding data for ICP-AES and ICP-MS are 78 and 47, respectively. Evidently, that potential of ETAAS is realized incompletely.

There are several reasons for situation like this, and first of all this is a mono-element character of ETAAS. However, problems with qualification of the analysts are significant as well. Methods of analytical chemistry present quite different demands to this point. For example, average analyst may receive moderate results using ICP-AES. Certainly, better analyst will obtain better results, but possibilities of this method towards solution of very difficult analytical tasks are quite limited. As for ETAAS, good specialists may solve unique tasks using this method (e.g., [47]). However, average analysts may fail even with relatively easy problem, especially being under time pressure. One may be sure that ETAAS needs closer cooperation between its users and the corresponding professionals.

РЕЗЮМЕ. Обсуждены современные тенденции развития различных областей атомно-абсорбционной спектроскопии (ААС). Предполагается, что наиболее важным направлением является развитие многоэлементной ААС и ее более широкое использование в практике. Применение методологии ААС с генерацией гидридов к элементам, которые не образуют летучие гидриды (Rh, Mn, Cd, и т.д.), является интересным при разработке чрезвычайно чувствительных методов анализа. Остаются актуальными работы по химическим модификаторам и разработка методов прямого анализа твердых проб. Важным является более широкое внедрение этих достижений в практику работы сервисных лабораторий за счет введения методов ААС в международные и национальные стандарты.

РЕЗЮМЕ. Обговорено сучасні тенденції розвитку різних галузей атомно-абсорбційної спектроскопії (ААС). Найбільш важливим напрямком є розвиток багатоелементної ААС та її більш широке використання у практиці. Застосування методології ААС з генерацією гідридів до елементів, що не утворюють летючі гідриди (Rh, Mn, Cd та ін.), є цікавим при розробці надчутливих методів аналізу. Актуальними залишаються роботи по хімічним модифікаторам і розробці методів прямого аналізу твердих проб. Важливим є більш широке впровадження цих досягнень у практику роботи сервісних лабораторій за рахунок введення методів ААС у міжнародні та національні стандарти.

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ПРОБОПОДГОТОВКА В РЕНТГЕНОФЛУОРЕСЦЕНТНОМ АНАЛИЗЕ ЖИДКИХ СРЕД

Обобщены результаты собственных исследований автора по пробоподготовке для РФА жидких сред и сопоставлены с общим состоянием этой проблемы. Показано, что наилучшими формами излучателей для анализа водных растворов являются получаемые из них в результате несложной термообработки квазитвердые излучатели на основе гелеобразующего агента (желатина или агара), полимерные стекла на основе сахарозы и полимерные пленки. Органические растворы могут быть превращены в органогели при помощи желатина и ПАВ или в тонкие пленки на основе подходящего полимера. Отмечены наиболее удобные и простые излучатели, которые легко сочетаются с разными вариантами предварительного аналитического концентрирования примесей, в частности, с низкотемпературной направленной кристаллизацией водного раствора.

Рентгенофлуоресцентный анализ (РФА) универсален по отношению к определяемым элементам, отличается избирательностью, имеет удовлетворительные метрологические характеристики, экономичен, легко поддается автоматизации, в случае портативных спектрометров сравнительно прост и недорог, рассчитан на многоэлементный контроль широкого круга объектов. В частности, РФА может применяться для контроля состояния природных вод и других жидких сред. Просмотрев около 700 ссылок по РФА, можно сделать вывод, что среди инструментальных методов для анализа вод чаще всего используются (в порядке убывания) спектрофотометрические, электрохимические, атомно-абсорбционные, атомно-эмиссионные методы, в том числе ICP AES, масс-спектрометрия, и, наконец, рентгенофлуоресцентная спектрометрия. В настоящей работе автор сделал попытку обобщить результаты своих собственных исследований по пробоподготовке к РФА жидкостей и сопоставить их с общим состоянием этой проблемы.

Поскольку длины волн рентгеновского излучения соизмеримы с межатомными расстояниями в кристаллических решетках, получаемые результаты из-за экранирования или рассеивания излучения неровностями или шероховатостями поверхности могут быть искажены, поэтому одним из основных требований РФА является использование анализируемых образцов (излучателей) с предельно гладкой рабочей поверхностью. Самым ответственным этапом любого, в том числе рентгенофлуоресцентного, анализа является пробоподготовка [1, 2]. Так, минимальное относительное стандартное отклонение РФА, рассчитанное из распределения Пуассона, составляет около 1 % [2]; но, как правило, реальные результаты анализа отягощены намного большей погрешностью. Кроме качества пробоподготовки, на результаты РФА существенное влияние оказывают физическое состояние образца и взаимодействие компонентов анализируемого вещества с рентгеновским излучением (матричный эффект) [3]. Степень такого взаимодейст-

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