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Atomic spectrometric detectors for flow-injection analysis

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ABSTRACT

The distinction between liquid chromatography and flow injection analysis is discussed in terms of the underlying concepts, the performance characteristics and the hardware involved. For the last aspect, attention is focused on the role of the detector and the development of spectroscopic detectors for these techniques is discussed. The limitations of atomic spectrometric detectors are discussed for the three most widely used techniques, flame atomic absorption spectrometry, plasma spectrometry and electrothermal atomisation atomic absorption spectrometry, and the recent literature concerned with the use of these techniques for chromatographic detectors is summarized. The use of flow-injection methods to extend the capabilities of the techniques, particularly as far as detection limits and matrix interferences are concerned, is discussed. These topics are illustrated by a detailed review of relevant papers from 1988 and 1989. It is concluded that there is a considerable sustained research effort in this field.

In the second edition of their book, Ruzicka and Hansen [1] offer the following definition of flow injection analysis (FIA): "Information-gathering from a concentration gradient formed from an injected, well defined zone of a fluid dispersed into a continuous unsegmented stream of a carrier". This definition differs from that offered in the first edition because in the intervening 7 years, the considerable versatility of an analytical methodology based on the controlled transport of determinant species and/or interdispersion with reagent species had become apparent. It has also become clear that FIA is more than an approach to the automation of serial assays. However, it has become apparent as more reports of multi-determination, of speciation studies and of the use of packed-bed reactors have appeared in the FIA literature that practitioners of FIA were in danger of reinventing liquid chromatography (LC).

The broad definition offered by Ruzicka and Hansen recognizes that the analytical methodology in which the key concepts are control of (a)

the sample volume and (b) the extent of on-line physical and chemical processes includes both LC and what was formerly regarded as FIA. In effect, the two techniques are subsets of all the techniques which are encompassed by the concept of "analyses in which a fundamental system parameter is fluid flow". The term "flow analysis" is not really appropriate, as by analogy with "trace analysis" (the determination of trace amounts), "water analysis" (the analysis of waters), etc., the term ought to be interpreted as the analysis of flows. However, the equally inappropriate term, flow-injection analysis (the analysis of injections into a flowing stream) will probably become universally adopted and thus it is likely that this area of analytical methodology will become known as flow analysis.

Although it may be difficult to formulate a definition of FIA that reflects the extreme diversity of the technique but which makes a conceptual distinction between FIA and LC, there is little difficulty in distinguishing between the two techniques when the operating hardware is ex-

aminated. This is true for pumps, injection valves and manifold components, but the two techniques converge again when detectors are examined.

DETECTORS FOR FLOW ANALYSIS

At the level of the hardware involved, there is considerable similarity between LC and FIA. As both are quantitative techniques, both need high-precision components. As both techniques are dynamic, in that processes occurring in the flow streams are such that the concentration of detected species is continuously varying, both need highly reproducible pumping and injection systems. Both techniques place demands on detector performance but for slightly different reasons. For both techniques it is desirable that the detector has high sensitivity, low noise, rapid response and a minimum contribution to mixing processes in the flowing stream. The first two factors contribute towards the detection limit obtainable by the particular analytical method, the second two contribute to the separation between successive peaks in the record of detector response vs. time. For both techniques it is necessary to be able to make quantitative measurements, usually of peak height for FIA and of peak area for LC, free from contributions from neighboring peaks.

In LC, the extent to which peaks are separated is related to the chromatographic parameters of capacity factors, solvent composition, nature of the stationary phase, flow-rate and temperature. However, it is not sufficient to obtain a good time separation between peaks. Quantification is possible only if neighboring peak widths are such that there is limited overlap. The width of LC peaks is due mainly to processes occurring within the column, such as flow tortuosity (or eddy diffusion), longitudinal diffusion and slow equilibration between mobile and stationary zones (resistance to mass transfer). The extent of broadening is also controlled by the parameters listed earlier. Naturally, an LC system is designed to minimize extra-column broadening effects due to flow through connecting tubing and detector cells and due to the injection process.

In a typical flow-injection procedure, the entire process may take place in open-tubular reactors and therefore, for systems in which on-line chemical derivatization is used, a certain amount of mixing between the injectate and reagent streams is necessary, so the system is designed to achieve the required degree of mixing. This mixing may be obtained from a combination of several different hydrodynamic regimes of which the flow patterns in the detector cell may be a major contributor. For example, high-sensitivity spectrophotometric procedures have been reported [2] in which the cell volume was 100 μl . Such a cell would be considered unusable for LC detection.

If the contribution to the mixing processes from the detector is negligible, suitable hydrodynamic regimes must be obtained from other components in the flow manifold. This is not normally a problem as it is considered that most manifolds, for spectrophotometric procedures at least, described in the literature produce an unnecessary degree of mixing [3]. Regardless of the extent of broadening produced by the various flow patterns between injection and detection it is always possible, in FIA, to adjust the conditions so that no overlap between adjacent peaks occurs by the simple expedient of varying the rate at which samples are injected. However, this does not mean that detector design for FIA is not an important consideration. In general, because of kinetic effects, it is better to ensure that the desired degree of mixing between the determinand and reagent species occurs before the reaction zone reaches the detector and hence the same design criteria for detectors for both LC and FIA may be considered to apply. The role of the detector in FIA has been examined [4,5] and in particular the practical effects of different spectrophotometric flow cell designs [6] have been discussed. The characteristics of detector performance for LC have also been considered in detail [7-9].

OPTIMIZATION IN FIA AND LC

Despite the differences in concepts between FIA and LC, there is considerable common ground when the factors controlling performance are con-

sidered. Reijn et al. [10] applied the results of Knox and co-workers [11,12] and of Guiochon [13], who considered LC systems, to FIA. It was concluded that in order to improve the performance in terms of throughput and reagent consumption while maintaining adequate residence times (to allow chemical reaction to occur to a measurable extent), FIA systems should be miniaturized. In common with LC, the limiting factor to such a miniaturization was identified to be the detector volume. The problems associated with miniaturization of detector volume were discussed by Poppe [14] for the techniques of molecular absorption in solution, molecular photoluminescence in solution and some electrochemical techniques. In the first technique, it was concluded, based on a consideration of the noise characteristics of the source and the detector, that it was not possible to reduce the volume much below 10 μ l without degrading the detection limit obtainable. This argument was based on a consideration of the number of photons that could be passed through the cell when a deuterium or low-pressure mercury lamp was used as the light source. It was further concluded that "for significant miniaturization of absorption detection systems, the use of lasers is inevitable". It was pointed out that techniques such as photoacoustic and thermal lens spectrometry could have applications in this area. Van der Linden [15] subsequently reiterated both the advantages of miniaturization and the limitations imposed by the difficulties in miniaturizing the detector volume.

ATOMIC SPECTROMETRIC DETECTORS

When viewed in the light of the criteria outlined above, atomic spectrometers appear singularly unsuitable as detectors. Unlike various forms of molecular spectrometry, notably UV and visible absorption spectrometry, for which considerable efforts have been made to design forms of the instruments specifically for use in on-line applications, there are no forms of atomic spectrometric instrumentation designed specifically for use in on-line situations.

TABLE 1
Commerically available types of atomic spectrometry

No.	Technique	Abbreviation
1	Flame atomic absorption spectrometry	FAAS
2	Electrothermal atomisation atomic absorption spectrometry	ETA-AAS
3	Inductively coupled plasma optical emission spectrometry	ICP-OES
4	Flame atomic emission spectrometry	FAES
5	Direct current plasma OES	DCP-OES
6	ICP mass spectrometry	ICP-MS
7	ICP atomic fluorescence spectrometry	ICP-AFS
8	Microwave induced plasma OES	MIP-OES

This situation exists possibly because (a) manufacturers do not perceive a sufficient market or (b) there has not been sufficient demand from users. The various types of atomic spectrometry which are commercially available are listed in Table 1. The first three are the most widely used at present. The use of technique 4 is probably declining, that of technique 5 is probably static, but techniques 6 and 7 are being increasingly used (particularly technique 6 ICP-MS) [16]. Technique 8 is only available commercially as a detection system for gas-liquid chromatography (GLC) and as such is demonstrating considerable potential [17].

The performance characteristics of FAAS are such that it requires milliliter sample volumes for a steady-state response. Although the technique will accept continuously flowing streams, the optimum flow-rate can be as high as 8–10 ml min⁻¹. Detection limits are typically at low mg l⁻¹ levels and the working range is short. The technique suffers from a considerable number of interference effects but the instrumentation is simple and robust. In some respects, ICP-OES is similar (milliliter sample volume and steady-state signals) but the uptake rates are slower (1–2 ml min⁻¹) and the working range is much longer with ng l⁻¹ detection limits. The technique has minimum chemical interferences but suffers from severe spectral interferences (depending on the matrix) and is not nearly as robust as FAAS. This latter comment applies to ETA-AAS also. Unlike the

other two techniques, ETA-AAS has intermittent operation, requiring a few microliters of sample every 2–3 min. This technique has the lowest detection limits of the three most widely used but has a short working range and is very prone to chemical interference effects.

The driving force behind the use of atomic spectrometric detectors for LC is the requirement to obtain information about element speciation at the trace level. This is particularly so in clinical and environmental studies in which the toxicities of element species are of interest. The appearance of a recent book related to this latter area (of which ref. 17 is a chapter) underlines the growing interest. The relevant literature has also been briefly reviewed for both LC [18] and GLC [19]. The former of these reviews cites 72 references, of which the largest group (24) is concerned with ETA-AAS. Flames account for a further 23 (19 AAS and 4 AFS), with ICP-OES accounting for 16 and DCP-OES for 9. A considerable variety of ways of connecting the liquid chromatograph and the atomic spectrometer together were described. Developments are continuously being reported; for example, one of the most recent interfaces to be considered for linking ETA-AAS with LC is the thermospray [20].

All of these devices are of potential interest in flow-injection atomic spectrometry. However, because flow-injection methods are designed primarily for the determination of just one component in a sample, it is more appropriate, when viewing the combination of techniques, to consider the combination as flow-injection introduction methods for atomic spectrometry with the overall aim of enhancing the performance of the particular atomic spectrometric technique in question. This view has one drawback in that it focuses attention away from poor characteristics of atomic spectrometers as monitors of transient events in continuously flowing streams. However, there is recent evidence that a number of researchers are actively pursuing the theme of modification of the instrument so as to improve performance in this respect [21–30]. A number of the modifications concern reduction in the volume of the spray chamber [22,25,27–29] whereas others are concerned with the use of a thermospray [20,21,24,26]

or heated spray chamber and desolvation [23,30]. Obviously there is a considerable overlap in the requirements of FIA and LC in this respect.

The continuing developments in this aspect of analytical atomic spectrometry may be followed in the regular review literature [31–34].

Flow-injection sample introduction for atomic spectrometry

Much of the first published work in the area of flow-injection atomic spectrometry was concerned with using the on-line dilution and limited sample volume features of flow-injection introduction [35]. These features were exploited in a number of ways to extend the concentration range of flame AAS and to handle samples incompatible with continuous nebulization into flames or plasmas such as those with a high dissolved solid content or chlorinated organic solvents. The former ability has recently been re-examined [36] by a manufacturer's laboratory as a prelude to the launch of a commercial flow-injection system for atomic spectrometry. It has also been shown to be a useful feature for ICP-OES [37] and ICP-MS [25,38]. The ability to control the extent of dispersion has been exploited for a number of calibration strategies involving both continuous and discrete dilution stages [39]. Early workers pointed out the possible benefits of having control over the sample introduction state by virtue of the pump. These included some removal of the variation in uptake rate due to variation in sample viscosity [40] and the ability to modify the nebulization efficiency [41].

This latter feature has developed into an area of some controversy as there have been suggestions that the use of conditions in which nebulization efficiency is increased (normally by reducing the flow-rate from the level that gives the maximum response) coupled with the use of peak-area measurement and/or the use of air compensation leads to improvements in signal-to-noise ratio and hence in detection limits [41–43]. However, these findings have not been confirmed by other workers. High flow-rates have been reported as beneficial [44], air compensation has been found to decrease precision [45] and detection limits have been found to be best under conventional operat-

ing conditions [46]. Some possible reasons for this divergence of views have recently been discussed [47,48] and it was suggested that the variations in experimental findings could be due to the variation in the performance of nebulisers and spray chambers of different designs and under different operating conditions. There has also been debate over the possible benefits of operation under starvation conditions in terms of reduced solute volatilization interferences. Some workers have reported such reductions [43,48] whereas others have found no benefits [49].

It is this area, namely that of control of interference effects, which has attracted most research effort recently. Often this has resulted from an effort to improve the working range at the lower concentration end. A number of methods for the implementation of the standard additions calibration method have been described [50–54] for the compensation of interference effects. The well known approach of vapor generation has also been converted to a flow-injection format for the determination of mercury [55–57] and the hydride-forming elements [58–60] and recently attempts have been made at the on-line removal of interferences [61]. Other volatile species which have been generated by on-line chemical reactions include methyl borate [62] (for overcoming the interference from iron in determination by ICP-OES), copper acetylacetonate [48] (to demonstrate the on-line generation of a volatile metal chelate for determination by FAAS) and nickel carbonyl [63] (for the determination of nickel in urine by MIP-OES).

However, the aspect of this area of interference removal in which there is most activity at present is the use of on-line chemistry for the separation of analyte and matrix species. The techniques used often result in an increase in the analyte concentration in the solution presented to the instrument and thus improve the performance of the conventional operation of the instrument at the lower concentration end of the calibration. There is considerable interest in three methods for matrix removal and preconcentration, namely liquid-liquid extraction, liquid-solid extraction and precipitation.

Liquid-liquid extraction

Manifolds for performing on-line liquid-liquid extraction (LLE) were first described in 1978 [64,65], although detailed treatments of the mechanisms and factors affecting the extraction process have appeared only recently [66,67]. Earlier applications of LLE with atomic spectrometry have been reviewed [35,47] and the problem of the mis-match in flow-rates for methods for use with FAAS has been noted. Efficient extractions are obtained at flow-rates considerably less than those which give good peak-height sensitivity. This has been overcome by using the flow-injection valve as the interface between a continuous flow LLE system and the spectrometer [68] and injecting the organic extract into a water carrier stream, and using a compensating flow of organic solvent [45,69]. More recently it has been shown that an increase in sensitivity could be obtained in comparison with the former approach by injecting the extract into an air carrier stream [70]. In this application, lead was determined in soil extracts by extraction with iodide into 4-methylpentan-2-one at an injection frequency of 60 h⁻¹. A 60-fold enhancement was obtained and the detection limit was 20 µg l⁻¹. Nebulizers for use with ICP instruments typically operate at much slower uptake rates than those for FAAS and hence the direct coupling of an FI-LLE system to an ICP spectrometer is possible. A method for the determination of beryllium in magnesium-aluminium and copper alloys based on this principle has recently been described [71] in which the analyte was extracted with acetylacetone into a stream of tetrachloromethane flowing at 0.7 ml min⁻¹. Separation of the phases was achieved by a 100-mm length of microporous PTFE tube (1 mm i.d., 2 mm o.d., 70% porosity and maximum pore size 3.5 µm). This type of separator has been used by other workers for on-line LLE with satisfactory results [48], but it appears to be less suitable than the flat PTFE membrane separator for gas-liquid separation (at least as far as the determination of arsenic by FI-hydride generation-ICP-OES is concerned) [60]. This type of separator was used in an indirect FAAS procedure for the determination of cationic surfactants in waters [72]. The analyte species were extracted as ion pairs with tetra-

thiocyanatocobalt(II) into 4-methylpentan-2-one in a continuous flow manifold and the organic extract (flowing at 0.36 ml min^{-1}) was injected ($130 \mu\text{l}$) into a carrier stream of water (flowing at 3.0 ml min^{-1}) and pumped to the nebulizer of the spectrometer. A sampling frequency of 35 h^{-1} was obtained at a precision of 1.2% (relative standard deviation) for 4.0 mg l^{-1} dodecyltrimethylammonium bromide solution. The detection limit was 0.13 mg l^{-1} .

Liquid-solid extraction

Since the first paper describing the use of an in-line column of solid reagent for the determination of some trace elements in sea water by a two-step procedure in which the metal removal step was followed by elution with an acid carrier stream [73], there has been a considerable increase in method development in this area [35,47]. Several different types of solid reagent have been used, some of which are commercially available [74] and some of which have been synthesized in the investigating laboratory [75].

Recently, the range of solid phases used has been extended by the development of methods incorporating silica-bonded strong anion and cation exchangers [76] (determination of vanadium by FAAS), various silica-bonded chelating agents [77,78] (determination of lead by FAAS) and a C_{18} bonded phase [79]. In the last method, lead and copper were determined by FAAS following retention of the metal diethyldithiocarbamate or quinolin-8-ol complexes and subsequent elution with methanol or ethanol, respectively. A brief summary of Chinese research in this area has been provided [70], in which the use of quinolin-8-ol immobilized on controlled-pore glass was applied to the determination of cobalt in various waters by FAAS and beryllium, cerium, cobalt, nickel and vanadium by ICP-OES. Problems encountered by earlier workers, arising from the shrinkage and swelling of Chelex-100 when the pH was changed during the elution and conditioning cycle of a packed column, has been overcome by the use of strong complexing agents as stripping agents [80]. L-Cysteine was found to be the best of those evaluated. The system was applied to the determination of copper in river water (with limited

success) as a part of a speciation manifold for the determination of cadmium, copper and zinc in natural waters in which a second column of AG MP-1 macroporous anion-exchange resin was used in series (and following) the Chelex-100 column. The system divided the sample into three fractions, that retained by the Chelex-100 (labile metal complexes), that retained by the anion exchanger (negatively charged metal species including humic acid complexes) and that not retained by either (inert neutral or positively charged complexes or metal associated with large colloidal particles which are excluded from the resin pores) [81].

A method in which segmentation of the sample solution during the preconcentration step by a stream of argon has been described for the determination of cadmium, chromium, copper, iron, lead, manganese and zinc by FAAS [82]. A complicated manifold was used in which, after the sample had been loaded onto the column (mounted directly on the nebulizer capillary), the liquid in the manifold between the solenoid valve and the nebulizer was blown out with a stream of argon. The solenoid valve was then switched to allow eluent (2 M nitric acid) to flow. If the liquid was not removed, poor precision was obtained and the peak height decreased with increasing distance travelled by the leading edge of the eluent stream. The effect was presumably due to dispersion effects at this leading edge which were absent in the case of a solution/gas boundary. Curiously, the effect was discussed in terms of diffusion during sample transport and of sample segmentation.

This manifold design, in common with others reported recently [83–85], allows the unretained sample components to flow through the nebulizer with the consequent risk of blockage in the case of samples with a high dissolved solid content. Two papers [84,85] described the use of activated basic alumina for the retention of lead (from a tap-water matrix) and cadmium (from a urine matrix).

The acidic form of this material was used to preconcentrate molybdenum from a sea-water sample prior to determination by ICP-OES [87]. An improvement in the detection limit by a factor of approximately 50 was obtained for a 50-ml sample volume. Elution was with $250 \mu\text{l}$ of 2 M ammonia solution. Molybdenum and tungsten

have been determined by plasma source ICP-AFS after preconcentration on an Amberlite IRA-93 anion-exchange resin and elution with 2 M ammonia solution in 70% (v/v) ethanol [87]. The ethanol suppresses the formation of metal oxides in the low-power atom source plasma.

The use of an in-line column has been applied to the removal of interferents prior to conversion of the analyte to a volatile hydride. Selenium was preconcentrated on a macroporous strongly basic anion exchanger [70] followed by elution with 1 M hydrochloric acid to give a detection limit of 2 ng l^{-1} at a sampling frequency of 50 h^{-1} . Nickel interference in the determination of arsenic has been overcome by the on-line removal of the nickel on a strong cation-exchange column [61].

The relative merits of some chelating resins for use in on-line preconcentration procedures for ICP-OES have been evaluated [88] and a detailed treatment of the design criteria for manifolds for liquid-solid extraction given [89].

A tubular cation-exchange membrane has been used for preconcentration and matrix modification by Donnan dialysis in the determination of lead in drinking water [90]. A 1-m length of 0.64 mm i.d. \times 0.89 mm o.d. Nafion 811, used as the injection loop of a rotary valve, was filled with acceptor solution (0.5 M strontium nitrate and 0.012 M aluminum nitrate in 0.1 M nitric acid) and immersed in the sample solution. After a 5-min dialysis period the acceptor solution was pumped to a flame atomic absorption spectrometer. The enrichment factor obtained, of the order of 100, was independent of sample ionic strength up to 10^{-2} M . A detection limit of $1 \text{ } \mu\text{g l}^{-1}$ was obtained.

Precipitation

Recently, one of the oldest analytical procedures, that of precipitation, has been used for on-line preconcentration and matrix isolation. Lead [91] have been determined in tap water by precipitation with hydroxide ion; copper [92] and cobalt [93] have been determined in rocks by precipitation with organic precipitants. For copper the reagent was dithiooxamide with dissolution in a solution of potassium dichromate in nitric acid. Both stainless-steel [90,92,93] and disposable nylon

membrane filters [94] have been used. An interesting feature of this approach is that other matrix components, which could compete with analyte species for binding sites on a solid extractant, may help improve precipitation collection efficiencies by means of coprecipitation.

Precipitation has also been used to remove the interference of aluminum in the determination of calcium [94,95] by precipitation of the calcium with basic ammonium oxalate. This reaction has also been used as the basis of an indirect method for oxalate [90].

This aspect of precipitation has been extensively developed by the Córdoba research group and indirect methods for oxalate, chloride and hydroxide [96], chloride and iodide [97], chloride [98] and components of various pharmaceutical preparations [99,100] have been developed. These latter methods include local anaesthetics [99] and sulphonamides [100].

Electrodeposition on a carbon felt electrode has been used to preconcentrate lead from tap-water samples prior to determination by both potentiometric stripping analysis and FAAS [101]. A sensitivity enhancement of up to 30-fold was obtained for five injections of 1.5 ml, allowing determination of lead in the $\mu\text{g l}^{-1}$ range. The possibility of using the system for speciation studies (only ionic forms of metals are sensed by the electrochemical detector) was discussed. A practical example of such speciation, using amperometry in conjunction with FAAS has been provided in the determination of iron(II) and iron(III) cyano complexes [102]. The method could handle 120 samples h^{-1} and had a detection limit of the species detected amperometrically of $1 \text{ } \mu\text{g l}^{-1}$. Both of these performance indicators were considerably superior to those of an ion-chromatographic procedure [103].

Interference effects and calibration

As many existing analytical methods which use atomic spectrometry as the instrumental stage suffer from interference effects in the measurement, method development procedures should be based on a good understanding of possible interference effects. A method for extracting information about interferences from the instrument re-

sponse at various instants across a dispersed injection profile in the absence and presence of potential interferents for ICP-OES has been devised [104]. The system was demonstrated for the investigation of the effect of excess concentrations of sodium on the emission from both atomic and ionic lines of calcium and magnesium. A computer-based data-handling facility produced response surfaces from which the magnitude of the interference could be readily quantified.

Interference effects in the determination of antimony by hydride generation AAS due to the presence of lead, tin, tellurium, arsenic, bismuth and selenium have been investigated [105] using a twin-channel flow system. The system could be used in two modes which differentiated between gas- and liquid-phase interferences.

Considerable efforts have been devoted to the development of flow-injection based calibration techniques [39], particularly the standard additions method, which has been implemented in a number of different ways. One of the most recent contributions in this area described a combined merging-zone zone-sampling manifold for the simultaneous determination of 19 elements in rock samples by ICP-OES by the generalized standard additions method [106]. In view of the authors' comments that the main factors affecting the calibration scheme were the operating conditions, it may be that a combination of this calibration method together with selection of operating conditions by the method mentioned earlier for quantifying interference effects [104] would produce the best accuracy and precision.

A simple network manifold with asynchronous merging of the split zones to produce overlapping peaks has been developed for the calibration of flame atomic absorption spectrometers [107]. It was also demonstrated that measurement at the minimum between the overlapping peaks from a suitably constructed two-branch network could give dilution factors of approximately 80.

Conclusion

There is a sustained interest in the interfacing of continuous flow sample-handling systems with atomic spectrometric detectors. These are signs that some consideration is being given to the

design of spectrometer modifications so that some of the inherent limitations on performance as chromatographic detectors are addressed. Although such design changes are of interest in FIA, it is the use of flow-injection techniques for sample preconcentration and matrix modification that is attracting most attention at present. There is no evidence that interest in the FI-AS combination is decreasing; on the contrary, the number of publications in the area is growing. If the appearance of a book gives a research area a certain respectability or indicates a certain maturity, flow-injection atomic spectrometry now satisfies this criterion [108].

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