

FROM THE LAB

Sample Dissolution

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Extensive experimental evidence indicates that variable and incomplete sample dissolution is one of the major causes of the inaccurate results being obtained widely in radiochemical analysis. This conclusion is easily demonstrated by analysis of the residues remaining after the sample has been leached. The residue often contains a significant fraction of the radionuclide being determined. Three procedures involving high-temperature fusions are recommended that ensure complete dissolution of virtually all types of inorganic samples routinely and reliably. With a few unique exceptions encountered over many years of constant use, dissolution of the entire matrix has been so complete that a Tyndall beam could not be observed when the solution of the final fusion cake was examined with a flashlight in a darkened room. Complete material balance studies using radioactive tracers have also shown no significant losses of even the large ter- and quadrivalent radionuclides that could be attributed to incomplete dissolution of high specific-activity particles of the most refractory and intractable species. The recommended fusion procedures are no more hazardous, time-consuming or difficult than other procedures giving much less complete or reliable dissolution.

Introduction

Elsewhere in the present issue of this Journal,¹ extensive experimental evidence from recent interlaboratory comparison studies was summarized showing that analytical performance of many laboratories is very poor and that overall performance has not improved significantly over the years.²⁻⁴ A recommendation was also made¹ that each laboratory implement a standard sample-analysis program in which samples containing known quantities of each nuclide of interest are analyzed routinely for quality control of the analytical performance of its own procedures and personnel. The advantages and disadvantages of various types of standards was discussed.¹ When the analyses indicate the presence of an unacceptable inaccuracy, steps can be taken immediately to identify the cause and develop suitable corrective action.

One of the most important—and most neglected—requirements of any acceptable analytical procedure is to ensure complete and reliable dissolution of the sample before accurate quantitative results can be expected to be obtained.²⁻⁴ Bowen and Volchok⁵ state: “To be useful for methods that involve only partial destructive attack on the sample, spiked standards must offer assurance that the constituents sought...respond to the analytical manipulations as do the same constituents in sample unknowns drawn from nature...” This statement is true but

not applicable in most cases because there is no way by which such assurance could be obtained, and there is no justification for such procedures to be used. Even prolonged treatment with boiling concentrated acids—as is widely practiced—cannot necessarily guarantee complete dissolution of most types of samples. Any procedure that fails to obtain complete sample dissolution for whatever reasons of economy, speed, sample load, or other expediency is untrustworthy at best, and will inevitably give low and erratic results. It is expected that incomplete sample dissolution is the primary cause of much of the erratic performance being observed in analytical work.

The large ter-, quadri-, and pentavalent elements are extremely hydrolytic, and form hydroxides, phosphates, silicates, carbides, etc. that are very insoluble and difficult to dissolve in the common acids, particularly if they have been heated strongly and converted to refractory forms. For example, eight samples of soil taken in the vicinity of a plutonium-handling facility were analyzed in the facility's own laboratory for ²³⁹Pu by their routine procedure involving leaching with nitric acid in the presence of ²³⁶Pu tracer. The insoluble residues were then analyzed for the same radionuclide by one of the present authors using a procedure involving complete dissolution in a potassium fluoride fusion in the presence of ²³⁶Pu tracer. Four of the residues contained more ²³⁹Pu than the corresponding

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leachates, three residues contained about half as much as the leachates, and only one contained as little as 22%, largely because that sample contained a relatively high activity of the radionuclide.² None of the water-soluble ²³⁶Pu tracer used in the original leach determination was present in any of the residues showing that heterogeneous exchange did not occur.³ The original results from leaching were therefore grossly inaccurate.

Use of hydrofluoric acid during leaching is very beneficial because of its strong complexing action on silica and most metals, but cannot guarantee by itself complete dissolution of the more intractable compounds.³ On four samples of soil containing from 0.04 to 20 dpm/g of ²³⁸Pu, Bishop et al.⁶ found: "Leaching and fusion results were essentially in agreement." Hydrofluoric acid was used in the leaching procedure. Yet, on a spiked soil standard containing ²³⁹Pu supplied to Bishop by one of the present authors, only 17% and 24% of the known content was removed by leaching despite the use of hydrofluoric acid. This standard sample had been ignited for four hours at 1000 °C during its original preparation to simulate the effect of strong heating, whether from a fire, a non-nuclear explosion, or deliberate ashing in a muffle furnace to destroy organic matter, as Bishop et al. actually did. They correctly identified the poor leachability to have been caused by the deliberate strong heating. However, their decision to use the leaching procedure routinely appears to involve a questionable assumption that refractory compounds will not be present in actual samples unless produced deliberately.

In many cases, the mono-, di-, and small trivalent elements can be leached fairly completely from simple solids by boiling with concentrated hydrochloric or nitric acids. However, even these elements cannot necessarily be guaranteed to be dissolved completely by selective leaching. If they are included in a refractory matrix, they will not be removed completely without dissolution of the matrix. If the samples have been exposed to water over long periods of time, such as with sediments in a radioactive waste pond, small ions such as divalent cobalt will have diffused deeply into the rock lattice from which they cannot be removed without complete dissolution of the host matrix. In contrast, because of its large size, ionic cesium has a marked tendency to undergo isomorphous replacement in the lattice of complex silicates from which it too cannot be removed completely. In some unpublished work by the present authors, 15% of the ¹³⁷Cs and 5% of the ⁶⁰Co in some pond sediments remained in the residue after extensive leaching, and could not be removed by further boiling for two hours with either concentrated nitric or hydrochloric acids. The fraction remaining in the residue was obviously much greater with shorter, more reasonable leaching times. Any time a residue remains to be discarded, there will always be doubt as to whether or not the radionuclide of interest had been removed completely.

It is also frequently assumed that because an isotopic tracer was used that exchange with the element being determined will be immediate and complete, and the accuracy of the analytical results thereby assured. Heterogeneous exchange between a water-soluble tracer and an insoluble form does not occur at a significant rate with refractory compounds.³ If complete sample dissolution is not achieved, use of isotopic tracers will not

result in accurate results because the tracer recovery will apply only to the portion dissolved.

On the other hand, if reliable procedures for complete dissolution of the sample are employed, the physical and chemical forms that existed in the original sample will have been destroyed and are irrelevant. However, there is no agreement even on what is meant by complete sample dissolution. In most cases, if most of the visible solid matrix disappears, sample dissolution is claimed to have been complete. However, in many cases, the procedure used for dissolution is strong enough to dissolve most of the sample matrix and yet leave an invisible residue of refractory material containing a large fraction of the carrier-free radionuclide being sought. Complete sample dissolution requires proof or irrefutable experience that the particular element or compound being determined was indeed converted to a soluble ionic form before expecting it to undergo chemical reactions characteristic of its species regardless of what happens to most of the visible sample matrix. Fortunately complete dissolution does not have to be proved experimentally on each sample, provided that a procedure is used that is intrinsically powerful and has been proved repeatedly to dissolve the most refractory and intractable materials expected to be encountered. Three such procedures involving high-temperature fusions have been used by the present authors for over 35 years on a wide variety of sample types such as soils, ores, tailings, minerals, sludges, incinerator ash, organics, etc. With very few unique exceptions, sample dissolution has always been complete when the prescribed procedure was followed.

Experimental

Potassium fluoride fusion

Fusion with anhydrous potassium fluoride in a platinum dish⁷ is probably the simplest, cleanest, and most effective and reliable method available for the rapid and complete dissolution of a wide variety of inorganic refractory and siliceous materials in a single operation. Potassium fluoride is available in high purity, and the fusion has virtually no effect on the platinum container, keeping contamination with foreign materials at a minimum. The high melting point of 858 °C and the high concentration of fluoride ion, which forms some of the most stable inorganic complexes known with silicon and many metals, both contribute to high rates of chemical attack on the sample. Thus, most metallic oxides as well as silica and refractory silicates are dissolved quickly and completely. Other alkali metal fluorides, including the acid and ammonium salts, are not effective because their melting points are either too high or too low, and their solvent capacity for metallic fluoride complexes is very poor. Three grams of anhydrous potassium fluoride is adequate to dissolve up to 1 g of most soils in a 50-mL platinum dish. With solids containing high concentrations of metals, smaller samples are advisable with 3 g of flux. Alternatively, 3.5 g of a mixed flux made by thorough blending of 100 g of anhydrous potassium fluoride, 70 g of anhydrous potassium hydrogen fluoride and 2 g of potassium nitrate has some advantages. It gives higher initial acidity and oxidizing power and eliminates the need for pretreatment of small samples with nitric acid,

making the mixed flux substantially faster for routine work. The platinum dish is placed on a triangle of heavy stainless steel wire on a ring stand and heated strongly over a blast burner with a 32-mm grid. When the flux is completely molten and clear, the dish is cooled with a slight rocking motion to distribute the cake slightly up the wall of the dish to minimize deformation of the dish. After cooling the cake, 4.0 mL of concentrated sulfuric acid is added and the mixture is heated to decompose the potassium fluoride cake with simultaneous elimination of both silica and fluoride by volatilization as silicon tetrafluoride and hydrogen fluoride. After the cake has been completely decomposed, 2 g of anhydrous sodium sulfate is added and the mixture is evaporated to a pyrosulfate fusion. Because pyrosulfate fusions are very corrosive to platinum ware, the fusion should not be heated any hotter or longer than is necessary to dissolve the salts and give a clear solution. The flux is cooled while swirling the dish gently to distribute the cake as uniformly as possible over the sides of the dish to facilitate its removal. After cooling, the sides of the dish are flexed to break the cake, and the cake is then added to 40 mL of boiling 1.5 M hydrochloric acid in a 100-mL Pyrex beaker. The beaker is covered with a cover glass, and the solution is boiled for five minutes to hydrolyze condensed phosphates and give a completely clear solution ready for analysis without filtration unless alkaline earth elements forming insoluble sulfates are present.

When larger samples are desired to obtain higher sensitivity and precision, the quantities of reagents and solutions used should be scaled up from those given by the same ratio as that of the sample size. The original procedure for 1-g samples of soil⁷ has been scaled up to 10-g⁸ and to 50-g samples.⁹ Recent descriptions give more details and several important improvements.¹⁰⁻¹² Color photographs of the entire procedure have been published.⁴ Samples of vegetation can be dry-ashed in borosilicate beakers overnight at about 550 °C, and an aliquot of the ash dissolved in a potassium fluoride fusion as described for soil. Provided only that the procedure was carried out correctly, sample dissolution has been demonstrated repeatedly to be reliably complete for both the sample matrix and individual particles of virtually all siliceous and refractory compounds, including high-fired oxides, phosphates, silicates, carbides, etc. of the large ter-, quadri-, and pentavalent elements.

Two important experimental conditions deserve additional explanation. When potassium fluoride is fused, the melt becomes progressively more alkaline with time due to slow but continuous volatilization of hydrogen fluoride produced by hydrolysis of potassium fluoride by water vapor. If moderate concentrations of metals forming very insoluble hydroxides such as iron, titanium, zirconium, etc. are present, and the fusion must be prolonged to dissolve intractable compounds completely, the alkalinity soon becomes high enough to override the solubility of the fluoride complexes and precipitate insoluble hydroxides. The normally clear and colorless melt becomes turbid, and dark brown in color if iron is present, and the dissolving action of the molten flux virtually ceases. Addition of 0.25 g of pure silica gel or silicic acid per 3 g of potassium fluoride flux rapidly restores the clear and colorless appearance of the melt on further heating, and dissolution of the insoluble

material resumes at its normal rate. The silica reacts with the hydroxyl ions to form metasilicate ions, thus reducing the hydroxyl ion concentration, the insoluble hydroxides dissolve and sample dissolution resumes.⁹ Obviously, small samples of soil of 1 g or less should not be pretreated with hydrofluoric acid. The silica normally present in soil extends the time available to achieve complete sample dissolution before precipitation begins and keeps the dissolution proceeding smoothly. Similarly, addition of a small quantity of silica is very beneficial during dissolution of samples containing significant quantities of metals and little silica such as sludges, water from rusty pipes, etc.

The other experimental condition deserving special explanation is the effect of alkali metal and sulfate ion concentration during the pyrosulfate fusion. During transposition of the potassium fluoride cake with sulfuric acid, the mixture becomes very thick due to precipitation of anhydrous metallic sulfates of iron, aluminum, calcium, etc., or their potassium salts, which are extremely insoluble in concentrated sulfuric acid. The thick mud retains sulfuric acid tenaciously and is almost impossible to evaporate to a pyrosulfate fusion without prohibitive spattering. However, if at least 2 g of anhydrous sodium sulfate is added per 3 g of potassium fluoride in the original fusion, the mixture changes on further heating to a very thin mixture of watery consistency that is easily evaporated to a pyrosulfate fusion without spattering. This effect is probably due to conversion of the insoluble anhydrous metal sulfates by the high concentration of sulfate ion added to anionic complexes that are soluble in concentrated sulfuric acid, particularly as their sodium salts. The resultant pyrosulfate cake then dissolves in dilute hydrochloric acid to give a completely clear solution. Even if a clear fusion can be obtained with potassium pyrosulfate alone, the resultant cake will frequently not dissolve completely in dilute hydrochloric acid if much iron, or particularly aluminum or chromium are present.

The chemical separations used with the fusion procedures must be applicable to solutions containing high concentrations of sodium and potassium sulfates. However, this has not been found to be much of a problem. For example, protactinium has a well-deserved reputation as one of the most hydrolytic and capricious elements known. It is very difficult to dissolve completely and to keep in ionic solution without depositing throughout the procedure. Using the potassium fluoride fusion, dissolution of protactinium ores has always been complete because of the powerful fluoride complexes produced with protactinium. Hydrolytic deposition throughout the subsequent separations has been completely eliminated because of the complexing action of the high concentration of sulfate ion present. After addition of concentrated hydrochloric acid, the protactinium can be extracted into diisobutylcarbinol with very high distribution coefficients without interference from the sulfates present.¹³ Similarly, acid solutions containing high concentrations of both potassium and sulfate ions are ideally suited for precipitation of minute quantities of uranium and the transuranium elements by barium sulfate by isomorphous replacement.^{8,9,11}

Pyrosulfate fusion

Fusion with an alkali pyrosulfate in a borosilicate glass Erlenmeyer flask is probably the most powerful, clean, simple and convenient method available for the rapid and complete dissolution of non-siliceous inorganic refractories. The flux is prepared simply by heating sodium or potassium sulfates, both of which are available in high purity, with a small molar excess of concentrated sulfuric acid until the excess sulfuric acid has been volatilized and a high-temperature fusion has been obtained. The sodium salt is generally preferred because of its higher melting point and the higher solubility of its complexes with most metals. Ammonium salts cannot be used because the low boiling point of ammonium hydrogen sulfate results in complete volatilization of the flux.

About 4.5 g of anhydrous potassium sulfate and 2 mL of concentrated sulfuric acid will suffice for 1-g samples of most soils, and gives the same final concentration of potassium sulfate as results from a 3-g potassium fluoride fusion. When potassium sulfate is not specifically desired (e.g., in anticipation of using barium sulfate separations) 5 g of anhydrous sodium sulfate should be used. The flask is heated over a blast burner carefully with continuous swirling to avoid breaking the flask or causing violent bumping of the solution until most of the excess sulfuric acid has been volatilized. As fast as is prudent, the temperature is increased until nearly the full heat of the blast burner is being applied. The melting point and dissolving action of the flux increase with strong heating almost to the softening point of the borosilicate flask so that as much heat as possible should be used without melting the flask. In fact, most problems with failures of pyrosulfate fusions to give complete dissolution result from application of too little heat or to use of too little flux. When the flux becomes clear, or no further dissolution occurs in the presence of siliceous material, the flux is allowed to cool while swirling the flask continuously to deposit the cake uniformly over the walls of the flask to minimize breakage. Forty milliliters of boiling 1.5 M hydrochloric acid is added and the solution is boiled for five minutes to hydrolyze condensed phosphates as with soil samples. When potassium is present (e.g., when potassium fluoride cakes have been transposed with sulfuric acid) sodium sulfate must still be added before the fusion to prevent formation of insoluble potassium salts with metals as discussed above. The cake is then dissolved in 1.5 M hydrochloric acid to give a completely clear solution ready for analysis. If siliceous materials are present, the sample is preferably dissolved initially in a potassium fluoride fusion in a platinum dish and then transposed with sulfuric acid as described above. If platinum ware is not available or cannot be used, the siliceous residue remaining from the pyrosulfate fusion is separated by centrifugation and dissolved separately as described in the following section.

Dissolution without use of platinum

There are several situations in which complete sample dissolution must be accomplished without use of platinum ware. Platinum ware is expensive and small laboratories might not be able to afford it. Platinum ware cannot be used with samples containing easily reducible metals such as lead, platinum met-

als, etc. which contaminate and embrittle the ware irretrievably. For example, dissolution of ash from incineration of radioactive organic wastes containing 372-d ^{106}Ru in platinum ware invariably contaminated the dishes permanently with high levels of activity. Dry-ashing of organic samples such as plastics, oils, tar, asphalt, paint, resins, activated carbon, plant and animal tissue, etc. in platinum ware can be very detrimental to the platinum, causing corrosion, recrystallization and embrittlement of the dish. However, dry-ashing of most organic materials is generally undesirable, even in containers other than platinum. Corrosion of the container with consequent loss of sample and cross contamination is severe, and the losses of nonvolatile components in the heavy, oily smoke evolved is unacceptable with certain types of samples such as plastics, rubber and petroleum products.

With soils or other inorganic samples, 5 g of anhydrous sodium sulfate and 2 mL of concentrated sulfuric acid are added to 1 g or less of the dry sample in a 125-mL borosilicate glass Erlenmeyer flask. While swirling the flask continuously, the mixture is evaporated to a high-temperature pyrosulfate fusion over the full heat of the blast burner. If a barium sulfate separation is to be used in the determination of the large trivalent and quadrivalent actinides, 4.5 g of potassium sulfate is used initially and 2 g of sodium sulfate is added after most of the excess sulfuric acid has been volatilized to ensure subsequent complete dissolution of metallic sulfates as described above. The pyrosulfate cake is boiled for five minutes with 40 mL of 1.5 M hydrochloric acid and transferred to a borosilicate glass centrifuge tube. After centrifuging, the supernate is decanted into another container. The residue is treated in the centrifuge tube with 1 mL of sulfuric acid, several drops of hydrofluoric acid and 0.5 g of sodium sulfate, and reevaporated to a pyrosulfate fusion. The cake is dissolved in 10 mL of 1.5 M hydrochloric acid, the solution is recentrifuged if necessary, and decanted into the container containing the main supernate. The combined filtrate is then analyzed as desired. The initial high-temperature pyrosulfate fusion dissolves all refractory oxides not associated with silica, and decomposes most of the remaining siliceous residues to forms that are more easily and completely dissolved by hydrofluoric acid during the retreatment. A procedure for determination of ^{210}Pb using this technique has been published.¹⁴

Most organic compounds should be wet-ashed to avoid serious physical losses which require use of powerful oxidants such as nitric and perchloric acids. Oxidation with nitric acid alone is either ineffective or produces serious fires, and perchloric acid inevitably produces violent detonations. Most organic materials must be charred thoroughly by strong heating with concentrated sulfuric acid to remove low-boiling flammable fractions prior to oxidation, and to decompose the complex materials to simpler ones more easily and completely oxidized before oxidation can be carried out safely and successfully. The charred material must then be oxidized with nitric acid until no further reaction occurs, with further charring with sulfuric acid as necessary, before perchloric acid may be used to eliminate the remaining organic matter. After most of the organic material has been oxidized, sodium sulfate is added to the

remaining sulfuric acid, and the solution is evaporated to a high-temperature fusion. The fusion should be heated with the full heat of a blast burner with a 32-mm grid as hot as the borosilicate glass flask will stand to facilitate complete oxidation of the last of the organic matter which is very resistant. The cake is dissolved in dilute hydrochloric acid, and the solution is analyzed as desired.

Statements frequently made that complete sample dissolution is generally unnecessary, and is undesirable because it is so time-consuming, expensive, and hazardous, are simply not true in most cases. Leaching procedures are very time consuming to obtain complete dissolution with refractory materials because they are relatively mild and require repeated lengthy periods of boiling with strong acids followed by filtrations, evaporations, etc. before chemical separations can begin. In contrast, a potassium fluoride fusion will dissolve most soils completely in 1 minute for a 1-g sample and only 6 minutes for a 10-g sample, about 4.5 minutes of which is required just to heat the 30 g of flux and 10 g of sample to its melting point. Transposition of the potassium fluoride cake with sulfuric acid to a pyrosulfate fusion with complete elimination of excess fluoride and silica produces a cake that is completely soluble in dilute hydrochloric acid ready for analysis, without having to be filtered or evaporated, and takes less than one hour for a 10-g sample. Statements that fusion procedures are more time-consuming than leaching procedures, or more hazardous than handling boiling concentrated acids are simply not in accordance with the facts. The most important consequence is that sample dissolution and tracer exchange are complete on every sample reliably, and losses occurring during subsequent chemical separations are corrected for automatically when tracers are used.

Hydrofluoric acid

The role of hydrofluoric acid in complete sample dissolution also needs some clarification. Although best known for its ability to dissolve silica, hydrofluoric acid also forms perhaps the most stable complexes with many heavy metals in acid solution of any inorganic complexing agent. Consequently, the rate of dissolution of refractory compounds of plutonium, thorium, and other elements that form fluoride complexes in acid is increased markedly in the presence of hydrofluoric acid. However, the fluorides of many metals commonly present in soils, such as calcium, lanthanides, and actinides, are also extremely insoluble and precipitate even in fairly strong acid, carrying the large ter- and quadrivalent elements extensively. After the solution has been evaporated to near dryness with nitric or perchloric acids to remove as much hydrofluoric acid as possible, boric acid should be added to complex the remaining fluoride and redissolve the insoluble fluorides.

For example,³ when a soil containing ignited $^{239}\text{PuO}_2$ was treated with excess hydrofluoric acid for an extended period of time, about half of the total plutonium remained in the insoluble residue. However, the ratio of ^{236}Pu to ^{239}Pu in the insoluble residue was the same as that in the soluble leachate showing that the refractory $^{239}\text{PuO}_2$ had dissolved and the soluble plutonium had been partly reprecipitated as the fluoride. The results were accurate because exchange with tracer was com-

plete and the losses in the residue were corrected for. Addition of boric acid to the acid solution of the residue dissolved the insoluble fluorides and decreased the quantity of both ^{236}Pu and ^{239}Pu left in the residue to less than 2%, thereby increasing the sensitivity and precision of the determination. Consequently, hydrofluoric acid can be used to obtain essentially complete dissolution of refractory compounds but the treatment must be prolonged, particularly in the presence of certain minerals not rapidly attacked by hydrofluoric acid. The lower rate of attack of hydrofluoric acid compared to potassium fluoride fusion can be readily appreciated by comparing its boiling point of about 110 °C and its ionization to fluoride ion of only a few percent to the melting point of 858 °C and complete ionization for potassium fluoride. During analyses of several hundred soil samples contaminated with plutonium from the crash of an aircraft carrying a nuclear device, Fowler et al.¹⁵ found that the results became lower and more erratic as the sample size was increased or the digestion time with hydrofluoric acid was decreased.

Conclusions

Even if the same result is obtained with a given leaching procedure as that obtained with complete dissolution on a given sample, there is no assurance that the same recovery will be achieved on any other sample as is frequently assumed. One can never know beforehand whether or not a given sample contains either the elements sought or the sample matrix in refractory form, and therefore whether or not a particular leaching procedure will be successful on that sample, regardless of its previous performance on another sample of presumably the same composition. The safest course for any laboratory striving for reliable analytical performance is to use a procedure that is known to dissolve completely the most refractory and intractable compounds expected to be encountered so that there is no insoluble residue remaining to be discarded. Whether or not such refractory particles are present in a given sample then becomes a matter of complete indifference. Analytical performance and laboratory reputation will both improve. In any event, it generally takes more time and effort to leach a sample completely, and to prove that the leaching was successful, than to use a total dissolution procedure to begin with.

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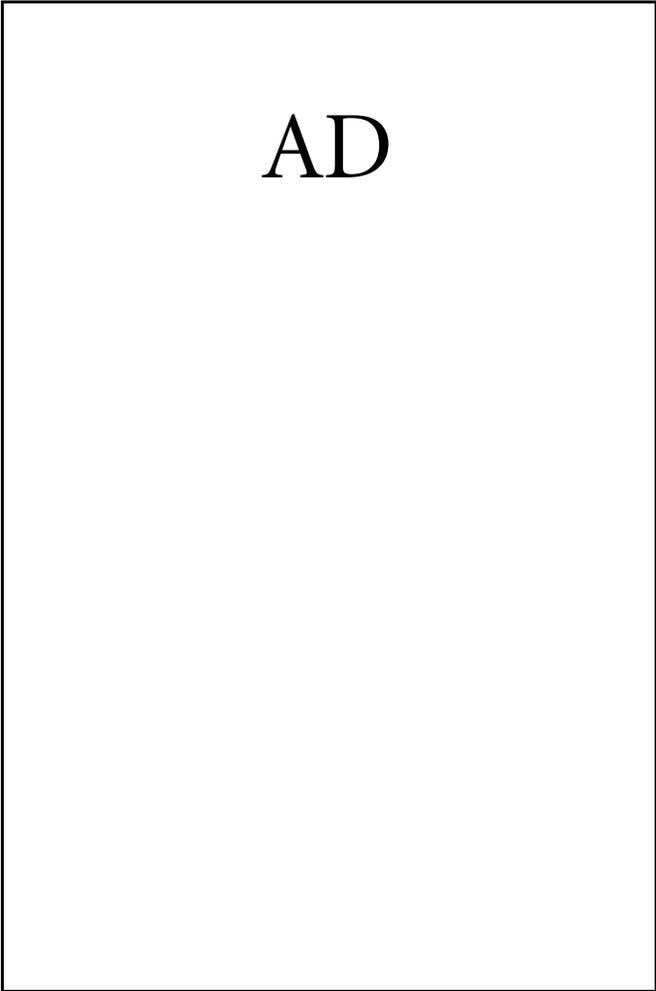
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