



Article Effects of Filter-Membrane Materials on Concentrations of Trace Elements in Acidic Solutions

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Abstract: Filtration is commonly used to separate liquids from solid materials before the determination of trace element concentrations in aqueous solutions. Therefore, it is important to determine how much elemental content is extracted from the filter itself or lost via absorption into the filter. In this study, we investigated three types of disposable syringe filters (polyvinylidene difluoride, PVDF; polytetrafluoroethylene, PTFE; PTFE with glass microfiber prefiltration media, GD/X) and their acid-cleaned versions using ammonium nitrate (NH4NO3) and acetic acid (HOAc) solutions. The concentrations of most trace elements (Li, Al, Cr, Mn, Co, Ni, Cu, Zn, Rb, Sr, Mo, Cd, Cs, Ba, Pb, and U) were higher in filtrates that had passed through acid-cleaned filters than those that had passed through uncleaned filters. In filtrates from PVDF and PTFE filters, many trace elements were below the detection limit. However, regardless of the filter type and acid cleaning, Li, Cu, Zn, Mo, and Ba concentrations in filtrates of NH4NO3 solutions, and Al, Cr, Mn, Cu, Zn, and Ba concentrations in filtrates of HOAc solutions were much higher than those of other trace elements. These differences were particularly noticeable in filtrates from GD/X filters containing glass microfiber layers. These data indicate that certain trace elements can be released from membrane materials by reacting with acid in the filtered solution. Furthermore, the amounts of each trace element were associated with the membrane type. These findings suggest that filter type should be carefully selected to obtain the required accuracy, in consideration of the target elements and whether an acid-cleaned filter is needed.

Keywords: trace elements; acid-cleaned filter; ammonium nitrate; acetic acid; membrane types

1. Introduction

Filtration is a common procedure used in the field and in laboratory settings to separate dissolved ions from suspended materials. Filter paper and syringe filters are the most commonly used filtration media. However, the use of filter paper is labor-intensive and often more time-consuming than that of syringe filters. Additionally, filtration through syringe filters requires relatively low sample volumes. Although these advantages have led to the widespread use of syringe filters, the type of syringe filter should be carefully selected because some of the raw materials used to manufacture filtration membranes can leach analytes into the filtrate [1].

A syringe filter consists of a housing that is typically made of polypropylene (PP) and a filtration membrane made from a wide range of synthetic materials. Representative types of membrane materials include polyvinylidene difluoride (PVDF), polytetrafluoroethylene (PTFE), PP, polyethersulfone (PES), nylon, and glass microfiber (GMF). The chemical compatibilities of these membranes differ among acids and bases, so it is important to select a filter that is compatible with the system to avoid an effect on the experimental results. For example, PVDF, PTFE, and GMF

membranes are resistant to acetic acid (HOAc), nitric acid (HNO₃), and hydrochloric acid (HCl), whereas PP and PES are not recommended for HNO₃ and PP has limited resistance to HCl [2].

To improve the analytical accuracy of methods that employ syringe filters, elements attached to the housing and membrane materials are often removed by acid cleaning [3–5]. Recently, Sakata et al. [6] suggested that filters should be pretreated via a heated acid cleaning process to decrease blank concentrations of certain elements. Using this filter pretreatment method and in consideration of the filter type, acid extractants (e.g., HNO₃) were passed through a variety of filter types. The resulting concentrations of trace elements in the blank solutions varied widely according to the filter material [1]. Many eluents can be used in liquid–solid separation, and it is important to determine the blank concentrations of trace elements resulting from the filtration process. Ammonium nitrate (NH4NO₃) and HOAc are common extractants used to determine dissolvable trace element contents in solid materials such as soil [7–10]. For example, in a recent study, exchangeable Sr fractions in soil were extracted with NH4NO₃ and HOAc to determine their concentrations and isotope ratios [11,12].

The objective of this study was to evaluate whether acid-cleaned filters are superior to uncleaned filters (i.e., new unused filters) in terms of experimental accuracy in determining trace metal concentrations when NH₄NO₃ or HOAc are used as the extractant, and to determine the most suitable filter material for each situation. We performed extractions using three syringe filter types. For each filter type, blank concentrations of trace elements in the filtrates were compared between uncleaned and acid-cleaned syringe filters.

2. Methodology

All laboratory equipment used in this experiment was prewashed with 10% HCl, rinsed three times with tap water and Milli-Q ultrapure water (MQW), and completely dried in a clean area at room temperature. The diluted HCl was prepared using 35~40% HCl (electronic grade; Chemitop, Chungbuk, Korea).

2.1. Reagents

NH₄NO₃ reagent (99.999% trace metal basis; Sigma-Aldrich, St. Louis, MO, USA) and HOAc (CH₃COOH, >99% optimal grade; Fisher Scientific, Hampton, NH, USA) were used in this experiment. The reagents were diluted with MQW containing 1 M NH₄NO₃ (80.04 g NH₄NO₃ in 1 L MQW) and 1 M HOAc (57.3 mL HOAc in 1 L MQW). These concentrations are typically used to extract cations from solid materials such as soil. The diluted solutions were stored in Teflon vessels until analysis. The dilution and filtering steps were carried out on the same day.

2.2. Syringe Filters

Three types of 0.45 μ m membrane syringe filters were evaluated in this experiment: PVDF, PTFE, and PTFE with GMF prefiltration media (GD/X). All filters were produced by the same manufacturer, eliminating any analytical errors due to differences among manufacturers. All filters featured a PP housing, were non-sterilized, and had a pore size of 0.45 μ m. According to the chemical compatibility of the membranes and housings [13], all filters were resistant to the acids HNO₃, HOAc, citric acid, and concentrated HCl. The GD/X filter consists of GMF 150 and GF/F layers produced from 100% borosilicate GMF on the top, with membranes formed of materials such as PVDF, nylon, or PTFE on the bottom. The GMF 150 layer retains particles sized 1–10 μ m in diameter, and the GF/F layer traps particles down to 0.7 μ m. The eluate from these prefiltration media flows directly onto the PVDF membrane filter. The PVDF and GD/X materials are hydrophilic, whereas the PTFE filter is hydrophobic.

2.3. Preparation of Acid-Cleaned Filters

For each filter type, three filters were acid-cleaned as follows. The filters were removed from sealed packages and soaked in a beaker containing 10% ultrapure HCl and approximately 30 mL acid was passed through the filters manually once. The filters were maintained in the acid solution

overnight at room temperature, without a change of acid, and then rinsed at least three times with tap water and MQW. To completely remove any remaining HCl, 50 mL MQW was manually pressed through each membrane. The filters were dried completely in a clean booth at room temperature.

2.4. Sampling and Analysis

The primary NH₄NO₃ and HOAc solutions were passed through the uncleaned and acid-cleaned filters using 10 mL syringes. Aliquots of approximately 1 g filtrate were directly transferred into 15 mL Falcon tubes on a microbalance (ME204, Mettler Toledo, Switzerland). This procedure was performed 10 times in parallel; thus, a total of approximately 10 g solution was extracted through each membrane filter and transferred into 10 tubes in 1 g fractions. Sampling was performed in triplicate for each filter type. Trace element contents (Li, Al, Cr, Mn, Co, Ni, Cu, Zn, Rb, Sr, Mo, Cd, Cs, Ba, Pb, and U) in primary acid solutions and filtrates were analyzed using inductively coupled plasma mass spectrometry (X-Series; Thermo Elemental, Cambridge, UK) at the Korea Basic Science Institute.

2.5. Changes in Filtrate Trace Elemental Concentrations

To quantitatively calculate changes in the trace element concentrations of both solutions after passing through the filters (loss or gain), the elemental concentrations were compared to those of each primary solution using the following equation:

loss or gain =
$$[(b/a) - 1] \times 100 (\%),$$
 (1)

where a and b are the concentrations of each trace element in the primary solution and filtrate, respectively.

3. Results and Discussion

Filtrate solutions were passed through three syringe filter types (PVDF, PTFE, and GD/X) with and without prior acid-cleaning. Table 1 lists the concentrations of 16 trace elements (Li, Al, Cr, Mn, Co, Ni, Cu, Zn, Rb, Sr, Mo, Cd, Cs, Ba, Pb, and U) in the resulting eluates. Trace elements were analyzed in the primary NH₄NO₃ and HOAc solutions, and Table 1 also lists their initial concentrations. Several trace elements were found in the primary NH₄NO₃ and HOAc solutions. For example, the primary NH₄NO₃ solution contained 56.1 μ g L⁻¹ of Mo and 18.4 μ g L⁻¹ Li. Al, Cr, Mn, Cu, Zn, and Ba were also present in amounts less than 10 μ g L⁻¹. In the NH₄NO₃ solution, Co, Ni, Rb, Sr, Cd, Cs, Pb, and U were below the limit of detection. In the HOAc solution, Al, Cr, Mn, and Zn were detected below 5 μ g L⁻¹. Other trace elements were not detected.

3.1. Trace Elements in NH4NO3 Filtrates

3.1.1. Filtrates from Uncleaned Filters

Filtrates obtained from the three filter types contained Zn (175–686 μ g L⁻¹) and Ba (32.3–1492 μ g L⁻¹) at very high concentrations compared to the primary solutions (Table 1). By contrast, trace elements such as Al, Co, Cs, and U were not detected in most samples, regardless of the filter type (Table 1). Rb and Pb were not detected in samples filtered through PVDF, and Pb was not found in PTFE filtrates. Filtrates from the GD/X filters contained Cr, Mn, Ni, Rb, Cd, and Pb at concentrations lower than 0.5 or 1 μ g L⁻¹. Among the detected elements, Mn, Cu, Li, and Mo had lower concentrations in the filtrate than in the primary solution, and the elemental concentrations were lower on average, within the range of –79.6% to –5.7%, based on Equation 1 (Figure 1). Similarly, Berg et al. [1] found that filtrates from PTFE filters tended to contain lower concentrations of most trace elements. Thus, trace element concentrations in NH₄NO₃ filtrates decreased after filtration due to a loss of elements to the filter material. Recently, Hedberg et al. [14] reported that trace metals, such as Zn and Cu, can be adsorbed by and interact with PVDF and PTFE membranes and that these elements in the released from the membrane during filtration. Therefore, higher concentrations of elements in

filtrates compared to the primary solution can be attributed to dissolution of the filter itself. Lower elemental concentrations in the filtrate can be attributed to the absorption or adsorption of elements into or onto the filter, respectively.

Elemente	Primary	Uncleaned filter			Acid-cleaned filter		
		¹ PVDF	² PTFE	³ GD/X	PVDF	PTFE	GD/X
Elements	solution	(n = 30)	(n = 30)	(n = 30)	(n = 30)	(n = 30)	(n = 30)
	Avg. ± SD	Avg. ± SD	Avg. ± SD	Avg. ± SD	Avg. ± SD	Avg. ± SD	Avg. ± SD
Ammonium nitrate (NH4NO3)							
Al	4.01 ± 1.67	BDL	0.27 ± 1.01	BDL	1.62 ± 4.72	1.57 ± 2.65	3.00 ± 8.37
Cr	0.50 ± 0.50	0.50 ± 0.13	0.67 ± 0.20	0.92 ± 0.80	0.80 ± 0.35	0.84 ± 0.24	1.17 ± 0.72
Mn	1.09 ± 0.06	0.22 ± 0.06	0.46 ± 0.21	0.36 ± 0.14	0.62 ± 0.07	0.93 ± 0.29	1.34 ± 0.93
Zn	8.74 ± 0.63	231 ± 46.0	175 ± 76.1	686 ± 537	10.1 ± 10.2	5.21 ± 2.93	3071 ± 3832
Li	18.4 ± 0.25	12.9 ± 0.31	17.4 ± 3.69	13.5 ± 0.54	19.0 ± 0.57	19.4 ± 0.85	18.3 ± 2.59
Cu	7.16 ± 0.57	5.31 ± 0.41	6.74 ± 1.16	5.88 ± 0.78	6.76 ± 0.45	8.37 ± 1.26	9.88 ± 3.01
Mo	56.1 ± 1.52	17.7 ± 0.45	25.7 ± 7.21	19.1 ± 1.05	28.4 ± 0.88	30.0 ± 1.41	27.6 ± 5.98
Ba	0.59 ± 0.09	32.3 ± 1.04	48.2 ± 13.1	1492 ± 1633	66.1 ± 1.34	93.4 ± 18.8	6564 ± 9687
Co	⁴ BDL	BDL	BDL	BDL	BDL	BDL	BDL
Ni	BDL	0.75 ± 0.27	0.96 ± 0.37	0.86 ± 0.45	1.90 ± 0.21	2.62 ± 0.67	1.57 ± 0.41
Rb	BDL	BDL	0.11 ± 0.10	1.45 ± 1.97	BDL	0.07 ± 0.37	1.59 ± 2.16
Sr	BDL	0.24 ± 0.09	0.32 ± 0.11	11.0 ± 8.96	BDL	0.11 ± 0.50	27.9 ± 36.3
Cd	BDL	0.25 ± 0.03	0.11 ± 0.13	0.26 ± 0.04	BDL	0.01 ± 0.04	BDL
Cs	BDL	BDL	BDL	BDL	BDL	BDL	0.29 ± 0.46
Pb	BDL	BDL	BDL	0.25 ± 0.38	BDL	0.02 ± 0.10	BDL
U	BDL	BDL	BDL	BDL	BDL	0.01 ± 0.06	BDL
Acetic acid (HOAc)							
Al	1.15 ± 0.17	0.95 ± 0.66	0.12 ± 0.51	306 ± 236	9.88 ± 3.40	6.92 ± 1.95	311 ± 228
Cr	3.32 ± 0.37	4.44 ± 0.34	4.54 ± 0.46	5.54 ± 1.19	5.86 ± 0.70	5.38 ± 0.64	8.47 ± 3.08
Mn	0.07 ± 0.12	BDL	BDL	0.62 ± 0.60	0.53 ± 0.15	0.41 ± 0.18	1.56 ± 2.11
Zn	4.74 ± 0.96	3.83 ± 2.80	7.56 ± 18.1	1675 ± 2044	68.2 ± 33.4	84.4 ± 6.11	$6450 \pm 12,129$
Li	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Cu	BDL	BDL	BDL	0.48 ± 1.04	0.70 ± 0.43	1.04 ± 0.21	2.21 ± 3.79
Мо	BDL	BDL	BDL	0.05 ± 0.16	BDL	0.24 ± 0.47	BDL
Ba	BDL	BDL	BDL	3188 ± 4365	0.51 ± 0.35	0.64 ± 0.34	$7353 \pm 14,568$
Co	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Ni	BDL	BDL	BDL	0.21 ± 0.58	BDL	BDL	BDL
Rb	BDL	BDL	BDL	0.56 ± 1.38	BDL	BDL	1.08 ± 1.96
Sr	BDL	BDL	BDL	24.2 ± 31.7	BDL	0.11 ± 0.49	42.0 ± 92.8
Cd	BDL	BDL	BDL	BDL	BDL	0.02 ± 0.13	BDL
Cs	BDL	BDL	BDL	0.08 ± 0.21	BDL	0.01 ± 0.07	BDL
Pb	BDL	BDL	BDL	0.32 ± 0.64	BDL	BDL	BDL
U	BDL	BDL	BDL	0.02 ± 0.02	BDL	BDL	BDL

Table 1. Concentrations of trace elements in ammonium nitrate and acetic acid extracted from three uncleaned and acid-cleaned types of filters (unit in μ g L⁻¹).

¹PVDF: polyvinylidene difluoride, ²PTFE: polytetrafluoroethylene, ³GD/X: PTFE with glass microfiber prefiltration media, ⁴BDL: Below Detection Limit.



Figure 1. Average percent gains (white zone) from the filters or losses (grey zone) to the filters of trace elements in NH₄NO₃ solution passing through uncleaned and acid-cleaned membrane filters of three materials (PVDF, PTFE, and GD/X), compared to those in the primary solution. Error bars represent standard deviation (SD). PVDF, polyvinylidene difluoride; PTFE, polytetrafluoroethylene; GD/X, glass microfiber prefiltration media.

3.1.2. Filtrates from Acid-Cleaned Filters

Filtrate concentrations obtained from acid-cleaned filters were higher than those from uncleaned filters for most of the detected elements (Table 1). Similarly, acid-cleaned filters increased the concentrations of trace element levels in the blank to a greater extent than uncleaned filters, likely due to acid-induced filter damage. In particular, Zn and Ba concentrations in filtrates from acid-cleaned GD/X filters were much higher than those from uncleaned filters, up to 49-fold for Zn and 103-fold for Ba. These results differ from those of a previous study, which reported that blank levels of certain trace metals (Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, V, and Zn) in the filtrate were lowered to their limits of detection after passing through filters (PVDF membrane with PP prefiltration media) that had been acid-cleaned with HNO₃ [15]. Additionally, according to the manufacturer, the membranes and housings of the three filter types are chemically compatible with concentrated HCl and HNO₃, and up to 5% HOAc [2].

The high trace metal concentrations detected in filtrates from acid-cleaned filters may be explained by (1) contamination of the 10% HCl and MQW that were used to rinse the raw filter, and (2) leaching of elements from the filter materials during acid cleaning. The first explanation is unlikely because all of the laboratory equipment used in this study was acid-cleaned using the same acid solution. Additionally, Zn and Ba were found in high concentrations in both uncleaned and acid-cleaned filters. The particularly high levels of trace elements in filtrates from acid-cleaned filters suggests that the second explanation is more reasonable. In a previous study [1], filtrates from different filter membrane materials (e.g., PTFE, PVC, polysulfone, polycarbonate, and glass fiber membranes) contained wide ranges of elemental concentrations following extraction with 0.2 M HNO3. In particular, the amounts of Zn and Ba in glass fiber membrane filtrates ranged from 11 to 36 μ g and from 15 to 44 μ g, respectively. These levels were much higher than those obtained using other membrane filters. For example, PTFE filtrates contained 0.003–0.018 μ g of Zn and 0.002–0.004 μ g of Ba per filter. Similarly, in the present study, high Zn and Ba concentrations were only observed in acid-cleaned GD/X filters, which contained GMF. Moreover, membrane-derived contamination can be mobilized during acid-cleaning procedures [14] and leach into the filtrate.

Among the other elements (e.g., Al, Cr, Li, Mn, Cu, and Mo) detected in the primary solution, Li concentrations in filtrates from PVDF and PTFE were slightly higher than those in the primary

solution (Table 1). Li concentrations were <6% higher than those of the primary solution. Similar increases in concentration were observed for Cu in filtrates from PTFE (<17%) and GD/X (<40%), and for Mn from GD/X (<23%) (Figure 1). The remaining elemental concentrations were lower than those of the primary solution. Additionally, Mo in filtrates from all filter materials decreased from -50.9% to -46.5%. These results indicate that either gain from or loss to filter materials affects some filtrate trace elemental concentrations.

3.2. Trace Elements in HOAc Filtrates

3.2.1. Filtrates from PVDF and PTFE Filters

Regardless of pretreatment, the concentrations of 10 elements (Li, Co, Ni, Rb, Sr, Mo, Cd, Cs, Pb, and U) in most HOAc samples that had been passed through PVDF and PTFE filters were below the detection limits. Mo was detected in some PTFE filtrates, and Sr, Cd, and Cs were found in several samples (Table 1). Mn, Cu, and Ba were not detected in samples that had been filtered through uncleaned filters. Only three elements (Al, Cr, and Zn) were detected in samples that had passed through uncleaned PVDF and PTFE filters (Table 1). Due to losses of Al (–17.4%) and Zn (–19.2%) to uncleaned PVDF filter materials, their concentrations were lower in the filtrates, whereas the filter contributed to an increase in Cr (33.8%) (Figure 2). In filtrates from PTFE, gains of Cr (36.6%) and Zn (59.4%) from the filtrates than in the primary HOAc solution. By contrast, several elements (Al, Cr, Mn, Cu, Zn, and Ba) were detected in filtrates from acid-cleaned PVDF and PTFE filters (Table 1). The elemental concentrations were as high as 60–80% for Cr, 500–760% for Al, 490–650% for Mn, and 1300–1700% for Zn, compared to those in the primary HOAc solution (Figure 2). As observed in the NH4NO3 solutions, filtrates obtained from acid-cleaned filters contained markedly elevated concentrations of trace elements (Table 1).



Figure 2. Average percent gains (white zone) from the filters or losses (grey zone) to the filters of trace elements in HOAc solution passing through uncleaned and acid-cleaned membrane filters (PVDF, PTFE, and GD/X), compared to those in the primary solution. The error bars represent SD.

3.2.2. Filtrates from GMF

The concentrations of 10 elements (Li, Co, Ni, Cu, Rb, Mo, Cd, Cs, Pb, and U) in many filtrates from uncleaned GD/X filters were below their detection limits. Only eight elements (Li, Co, Ni, Mo, Cd, Cs, Pb, and U) were below their detection limits in filtrates from acid-cleaned filters, and even fewer (Ni, Cu, Rb, Mo, and Cs) were below their detection limits in filtrates from uncleaned filters after sampling (~4 g). Close examination of three individual acid-cleaned filters revealed that Rb was

detected in all filtrates from one of the filters, but was not detected after the third sampling from the second filter. Rb was not detected in filtrates from the third filter (Figure 3). Similar results were obtained for Pb in NH₄NO₃ filtrates from uncleaned filters (data not shown). These results indicate

that elements that originate from the membrane are not uniformly extracted from every filter.



Figure 3. Variation in Cr, Mn, and Rb concentrations in filtrate passed through uncleaned and acidcleaned filters. Samples were sequentially collected from 1 to 10 g.

Compared to other filters, filtrates from both uncleaned and acid-cleaned GD/X filters contained significantly higher concentrations of Al, Cr, Mn, Zn, Sr, and Ba (Table 1). Filtrates from the acidcleaned GD/X filters also contained high levels of Cu. In particular, Al, Zn, Ba, and Sr concentrations were much higher than those of PVDF and PTFE filtrates, by up to four orders of magnitude (Table 1). Compared to Al, Cr, Mn, and Zn detected in the primary HOAc solution, elemental concentrations in filtrates from both uncleaned and acid-cleaned GD/X filters were as high as 26,400–26,900% for Al, 65–160% for Cr, 790–2100% for Mn, and 35,200–136,000% for Zn, compared to those of the primary HOAc solution (Figure 2). Considering the trace element concentrations in the primary HOAc solution, as well as those in the PVDF and PTFE filtrates, these results indicate that large amounts of material are extracted from GMF-layered membranes. Thus, GMF-layered filters are unsuitable for separation of acidic liquids from solid materials.

3.3. Variation in Elemental Concentrations during Sequential Extraction

Regardless of acid pretreatment, elemental concentrations in both NH₄NO₃ and HOAc filtrates that had passed through PVDF and PTFE filters showed little change from those of the primary solution. By contrast, the levels of certain elements in uncleaned and acid-cleaned GD/X filtrates were high in the first few sample aliquots, and then gradually decreased with sequential sampling (Figure 3). Decreases in Cr, Mn, and Rb concentration are shown as representative examples; these decreases were more pronounced in filtrates from acid-cleaned GD/X filters. These results support our hypothesis that certain elements are leached from the raw materials used in GD/X filters and that acid-induced damage during acid-cleaning further exacerbates this problem. Furthermore, when approximately 3–4 g samples of the acidic solutions were passed through the uncleaned GD/X filters, concentrations of trace elements in the filtrate dramatically decreased to approximately the levels of the blank, suggesting that a flushing step should be conducted to prevent the gain of trace elements from uncleaned GD/X filters when filtering an acidic solution.

3.4. Filter Selection

Based on the results of this study, filters should be carefully selected to avoid contamination from the filter itself. For example, exchangeable Sr and carbonate Sr fractions in soil have been extracted using NH4NO3 and HOAc, respectively, to determine Sr isotope ratios [11,12,16,17]. After incubating the soil samples in each of the extraction solutions, the samples were filtered to separate the liquid from the solids. Considering that Sr and Rb were not detected in the primary NH₄NO₃ and HOAc solutions, PVDF would be the best choice of filter material for these chemical and isotopic analyses. Rb concentrations were below the detection limit with both uncleaned and acid-cleaned filters (Figure 3, Table 1), and only small amounts of Sr (0.05–0.43 μ g L⁻¹) were detected in filtrates from uncleaned filters (Figure 4, Table 1). Alternatively, an acid-cleaned PTFE filter may be used to analyze Sr concentrations and isotopic ratios, as long as the filter membrane is rinsed with a small amount of sample, although this was an inadequate strategy for uncleaned filters (Figure 4, Table 1). Most filtrates from uncleaned PTFE filters contained Rb and Sr concentrations of <0.5 µg L⁻¹. Glassbased membrane filters, both uncleaned and acid-cleaned, were deemed unsuitable for analyzing Sr concentrations and isotope ratios, although the concentration decreased sharply after flushing with ~4 g fractions (Figure 4); for example, NH4NO3 filtrates from uncleaned and acid-cleaned GD/X filters had mean Sr concentrations of 6.91 ± 2.11 and $7.08 \pm 2.48 \ \mu g L^{-1}$ for 5–10 g fractions, respectively, and HOAc filtrates included the Sr concentrations of 8.51 ± 2.69 and $8.11 \pm 2.59 \ \mu g \ L^{-1}$, respectively. Thus, Sr and Rb concentrations in the filtrates were much higher than those in the primary solutions (Figures 3 and 4). We strongly recommend that PVDF and PTFE filters be used when separating bioavailable Sr fractions from soil mixtures.



Figure 4. Relative increases in the average Sr concentrations in (**a**) NH₄NO₃ and (**b**) HOAc solutions passing through uncleaned and acid-cleaned filters, compared to those in the primary solutions, and (**c**,**d**) variation in their concentrations in GD/X filtrates during sequential extraction from 1 to 10 g.

4. Summary

In this study, we evaluated PVDF, PTFE, and GD/X syringe filters for use in trace element quantitation in solutions containing strong acid, NH₄NO₃, or HOAc. Half of the filters were

uncleaned and the rest were pretreated by acid cleaning with 10% HCl. Regardless of the type of filter or solution, filtrates that had passed through GD/X filters contained much higher concentrations of trace elements (Li, Al, Cr, Mn, Co, Ni, Cu, Zn, Rb, Sr, Mo, Cd, Cs, Ba, Pb, and U) than those that had been passed through other filter types. Overall, regardless of filter type, filtrates from acid-cleaned filters contained higher levels of trace elements than those from uncleaned filters. By contrast, trace element concentrations in filtrates from PVDF and PTFE filters were below their detection limits. These results suggest that PVDF- and PTFE-based filters are more suitable than GD/X filters for extracting trace elements from solid materials using acid. However, specific elements (Sr and Rb) were below their detection limits only when acid-cleaned PVDF filters were used. Therefore, GD/X filters should be carefully selected according to the purpose of the experiment. Based on sequential extractions using GD/X filters, removing the initial 3–4 g of filtrate may solve the problem of trace elements being released from membrane materials through a reaction with the acid solution.

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