

# Revealing a 5,000-y-old beer recipe in China

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**The pottery vessels from the Mijiaya site reveal, to our knowledge, the first direct evidence of in situ beer making in China, based on the analyses of starch, phytolith, and chemical residues. Our data reveal a surprising beer recipe in which broomcorn millet (*Panicum miliaceum*), barley (*Hordeum vulgare*), Job's tears (*Coix lacrym-jobi*), and tubers were fermented together. The results indicate that people in China established advanced beer-brewing technology by using specialized tools and creating favorable fermentation conditions around 5,000 y ago. Our findings imply that early beer making may have motivated the initial translocation of barley from the Western Eurasia into the Central Plain of China before the crop became a part of agricultural subsistence in the region 3,000 y later.**

Yangshao period | alcohol | starch analysis | phytolith analysis | archaeological chemistry

In China, the earliest written record of beer appears in oracle bone inscriptions from the late Shang dynasty (ca. 1250–1046 BC) (1, 2). According to the inscriptions, the Shang people used malted grains, including millets and barley/wheat (barley and wheat are represented by the same Chinese character, *lai*) as the main brewing ingredients (1, 3). Scholars have hypothesized that the Shang tradition of beer brewing has its origin in the Neolithic Yangshao period (5000–2900 BC), when large-scale agricultural villages were established in the Yellow River valley (4–6). The hypothesis is possible, considering that China has an early tradition of fermentation and evidence of rice-based fermented beverage has been found from the 9,000-y-old Jiahu site (7). Certain types of Yangshao vessels, including funnels and *jiandiping* (pointed-bottom vessel) amphorae, show stylistic similarities to the brewing equipment in the historical period and modern ethnographic records (6). However, direct evidence for alcohol production from Yangshao sites is lacking.

The Mijiaya site is located on a primary terrace northeast of the Chan River, a tributary of the Wei River, in Shaanxi, North China (Fig. 1 and *SI Text*). The excavations revealed two subterranean pits with artifacts that appeared to resemble in situ beer-brewing facilities (8) (Fig. 2 and Fig. S1). Both pits belong to Banpo IV (or late Yangshao period) stratum, and an established chronology based on ceramic typology and <sup>14</sup>C dates in the region securely places the time period between 3400 and 2900 BC (9, 10). Pit H82 was 3.7-m deep with straight walls and five steps leading down to the bottom (Fig. 2A); Pit H78 was 2.5–2.7 m deep with a flat bottom and a secondary platform on one side of the walls (8). Three types of vessels were recovered in both pits: wide-mouth pots, funnels, and *jiandiping* amphorae (Fig. 2B–D), all of which have yellowish residues on their interior surface (Fig. S2). The shapes and styles of the vessels suggest three distinctive stages in the beer-making process: brewing, filtration, and storage. Interestingly, each pit also contained a pottery stove (Fig. 2E). In brewing activity, heating equipment is often used to maintain the optimal temperature for mashing. The stoves would have been especially suitable for this operation. Our hypothesis is that the artifact assemblages exclusively from the two pits represent a “beer-making toolkit.” To test our hypothesis, we conducted starch, phytolith, and chemical analyses on the residues from two

complete funnels and pottery sherds from five *jiandiping* amphorae and two wide-mouth pots.

## Taxonomical Identification

The identification of starch grains and phytoliths was based on morphological and morphometric analyses. The morphological identification relied on a reference collection from over 1,000 Asian and European economically important plant specimens, and by consultation with published literature (11–16) (Table S1). For morphometric analysis, we applied two computer-assisted methods. First, a discriminant analysis model was used to separate the starch grains of Job's tears (*Coix lacrym-jobi*) from those of millets (*Setaria italica* and *Panicum miliaceum*). Based on three variables, including size, eccentricity of the hilum, and presence or absence of curved arms on the extinction cross, this multivariate model has a success rate of 82.4% for separating Job's tears from millets (17). Second, we conducted a morphometric analysis of the articulated dendritic phytoliths. Dendritics are produced in the inflorescence bracts of many common cereals, especially Triticeae species. Articulated dendritics produce wave patterns of taxonomic significance. Recent research has achieved good success at identifying wheat and barley phytoliths and distinguishing them from the relevant wild grasses (12, 13). A sample size as small as 30 dendritic wave lobes can be adequate for a 90% confidence level in discriminating among taxa based on differences in several wave lobe-shaped morphometrics. We measured the wave lobes of articulated dendritic phytoliths from six Mijiaya residue samples following the procedures outlined by Ball et al. (18). Each residue sample yielded at least 30 measurable wave lobes in total, which allowed us to have statistical confidence in the measurements of form factor, roundness, convexity, solidity, compactness, and aspect ratio (Table S2). We compared the means of these six morphometrics for the Mijiaya dendritics from each sample with the range of means observed in 20 Triticeae and other dendritic-producing species, including common

## Significance

**This research reveals a 5,000-y-old beer recipe in which broomcorn millet, barley, Job's tears, and tubers were fermented together. To our knowledge, our data provide the earliest direct evidence of in situ beer production in China, showing that an advanced beer-brewing technique was established around 5,000 y ago. For the first time, to our knowledge, we are able to identify the presence of barley in archaeological materials from China by applying a recently developed method based on phytolith morphometrics, predating macrobotanical remains of barley by 1,000 y. Our method successfully distinguishes the phytoliths of barley from those of its relative species in China.**

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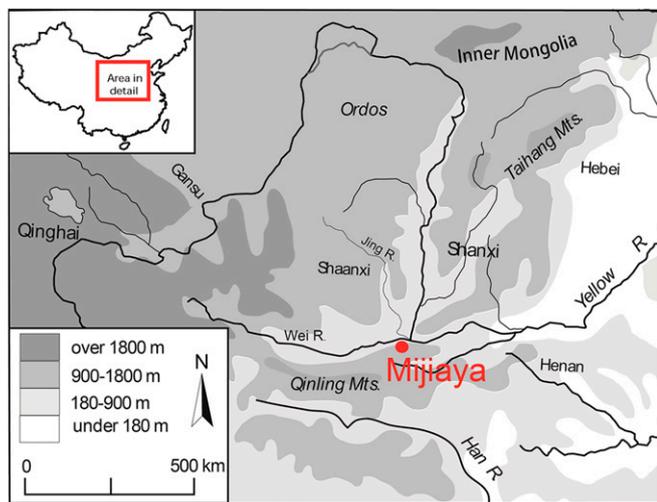


Fig. 1. Geographical Location of the Mijiaya Site.

wild species indigenous to China and domesticated species introduced into China from Western Eurasia (Tables S3 and S4).

## Results

A total of 541 starch grains were recovered from the funnels and pottery sherds (Table 1). Of these grains, 488 starch grains (90.2% of the total) were identifiable to various taxonomic levels compared with our reference data. The starch assemblage mainly consists of millet, Triticeae, and Job's tears, with a smaller contribution from tubers that include snake gourd root (*Trichosanthes kirilowii*), yam (*Dioscorea* sp.), and lily (*Lilium* sp.) (Fig. 3 A–F). A high percentage of starch grains ( $n = 166$ , 30.7%) exhibit signs of damage, and among them two types of damage closely resemble that produced by beer brewing. First, some grains show pits and channels on their surface, ranging from being slightly pitted to completely hollow (Fig. 4A). Second, a large number of starch grains are swollen, folded, and distorted (Fig. 4B); some still retain their individual boundaries, but many merge into one another. These two damage patterns precisely match the morphological changes developed during malting and mashing, as we observed in our brewing experiments and that reported in published literature (Fig. 4 C and D, Fig. S3, and SI Materials and Methods) (19–22). During malting, enzymes in sprouting cereals break down starch to dextrins and simple sugars, creating typical surface pits and interior channels in the grains (19). Furthermore, mashing involves heating of the malt in water for a period, which causes gelatinization, swelling, folding, and distortion of starch grains (19). Thus, the damaged state of the starch grains in our archaeological sample provides strong evidence for the conclusion that those starch grains are residues from the brewing process.

Phytolith data indicate the presence of cereal husks (Table 2). Phytoliths identified to the Panicoideae grass subfamily predominate the assemblage. Seven vessels revealed η-shaped long cells that are consistent with phytoliths formed in epidermal husk tissues of broomcorn millet (Fig. 3J) (15). Cross-shaped phytoliths showing a considerable variation in form and size, comparable with the crosses produced by Job's tears in our modern references, were observed (Fig. 3H). Phytolith forms produced in Pooideae were also identified. In particular, articulated dendritic phytoliths consistent in pattern and shape with those produced in the husks of Triticeae species were observed (Fig. 3K). Our morphometric analysis of the articulated dendritics indicates their most probable origin to be from the inflorescence bracts of barley (*Hordeum vulgare*). Although some of the mean measurements of the archaeological samples fall within the ranges of other taxa, all of the means

fall within those observed in *H. vulgare* (Tables S5 and S6). The profile of phytoliths corroborates the starch grain assemblage, indicating the presence of broomcorn millet, Job's tears, and barley.

Our ion chromatographic (IC) analysis identified the presence of oxalate, which develops during the steeping, mashing, and fermentation of cereals (23). Calcium oxalate is a principle component of “beerstone,” which settles out at the beer fermentation and storage containers, and has been used as a compound marker for identifying barley beer fermentation in ancient vessels (24–27). We conducted tests on the residues from Funnel 1, Pot 3, and Pot 5. The results confirmed that high levels of oxalate are present in Funnel 1 and Pot 5 (Fig. 5). Oxalate was not detected from Pot 3. The oxalate concentration is 0.08% (80 mg/100 g) for Funnel 1 and 0.05% (50 mg/100 g) for Pot 5. Although oxalates occur naturally in plants like spinach (*Spinacia oleracea*), rhubarb (*Rheum rhabarbarum*), and some *Dioscorea* and *Lilium* species, the vessel types in this study are not suitable for storing any fresh plant.

To rule out the potential contamination from the enclosing soil matrix and postexcavation conditions, we analyzed four samples as control specimens. Three samples were analyzed for starch and phytolith, including one from the sediment adhering to the exterior surface of Pot 5 (control sample 1), one from a stone adze fragment recovered from Pit H78 (control sample 2), and one from the plaster material used for reconstructing Funnel 2 (control sample 3) (Fig. S1). Compared with ancient samples, the control samples contained a much smaller number of phytoliths and starch grains (Tables 1 and 2) with no signs of damage. IC analysis of the exterior scrapings from Pot 5 (control sample 4) detected no oxalate, a result in clear contrast to a high level of oxalate found in the interior surface of the same vessel. These observations suggest that the high concentrations of starch, phytolith, and chemical residues related to the beer-making process are exclusively present on the interior surfaces of the Mijiaya vessels, which potentially have had direct association with beer brewing.

## Discussion and Conclusion

All three lines of evidence are consistent with the archaeological data, indicating that the Yangshao people brewed a mixed beer with specialized tools and knowledge of temperature control. Our data show that the Yangshao people developed a complicated fermentation method by malting and mashing different starchy plants. Compared with millets, barley has much higher α- and β-amylase activities, which promotes the saccharification process (28). Tubers

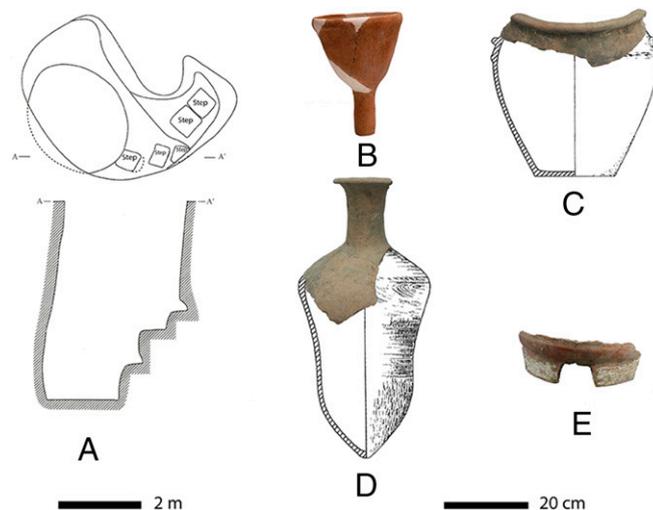


Fig. 2. The “beer-making toolkit” from Mijiaya Pit H82: (A) Pit H82 illustration in top and cross-section views, (B) funnel 1, (C) pot 6 in reconstructed form, (D) pot 3 in reconstructed form, and (E) pottery stove.

**Table 1. Counts of starch grain types from vessels**

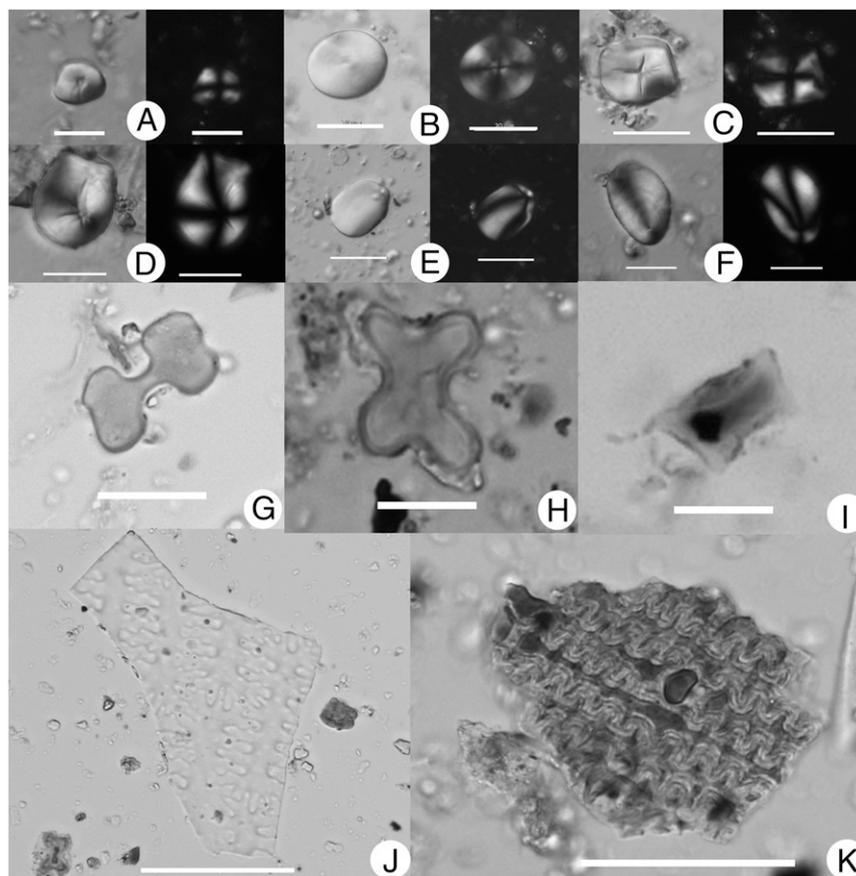
Artifact no.	Triticeae	Job's tears, <i>C. lacryma-jobi</i>	Millet, <i>P. miliaceum</i>	Snake gourd root, <i>T. kirilowii</i>	Lily, <i>Lilium</i> sp.	Yam, <i>Dioscorea</i> sp.	Tuber*	UNID	Total	Damaged
Funnel 1	24	49	78	0	0	0	0	7	158	47
Funnel 2	23	13	11	4	0	1	2	4	58	19
Pot 1	17	6	3	1	0	0	10	3	40	6
Pot 2	7	3	3	0	0	1	0	1	15	14
Pot 3	11	5	11	0	0	0	1	9	38	23
Pot 4	39	17	23	2	3	1	6	6	98	20
Pot 5	11	19	14	9	0	0	7	4	66	17
Pot 6	14	10	7	0	1	0	4	14	50	15
Pot 7	6	6	4	0	0	0	1	5	24	5
Total	152	128	154	16	4	3	31	53	541	166
Percent, %	28.61	23.7	28.5	3.0	0.7	0.6	5.7	9.8	100.0	30.7
Control sample 1	1	0	0	0	0	0	0	2	3	0
Control sample 2	3	0	0	0	0	0	0	3	6	0
Control sample 3	0	0	0	0	0	0	1	3	4	0

\*A general category that includes snake gourd root, lily, and yam. UNID, unidentified.

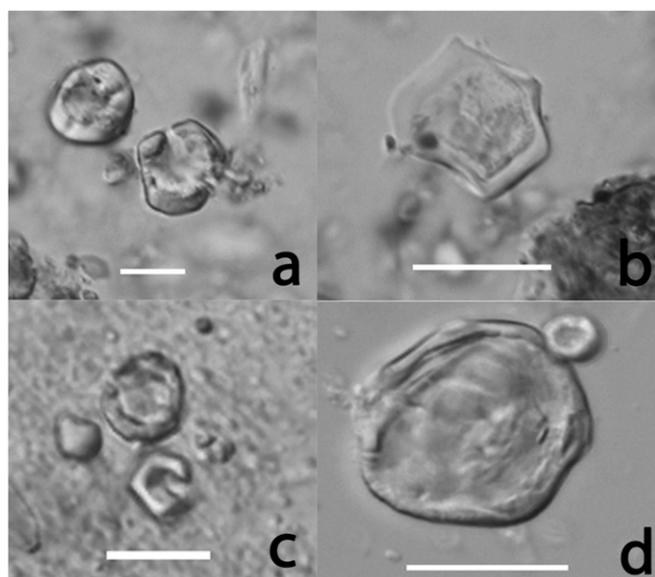
contribute starch and sugars for fermentation, and they also add a sweeter flavor to the beer. The Yangshao people probably developed their recipe through repeated experiments.

The discovery of barley in the beer residues suggests a social motivation in the initial stage of crop translocation (29). Barley was first domesticated in Western Eurasia and later introduced into China, presumably through the Central Asian steppe. The timing and nature of the crop's initial adoption in China is still

not well understood (29–31). In the Central Plain, macrobotanical remains from the Yangshao sites are generally well preserved, dominated by millets and very few other cereal types, and no evidence of barley has been reported. The earliest evidence of barley comes from some sporadic finds in Bronze Age sites, all dated around or after 2000 BC (31, 32). Not until the Han dynasty (206 BC–AD 220), three millennia after Mijiaya, had this crop become an important part of



**Fig. 3.** Starch and phytolith types from Mijiaya vessels (the starch types showing DIC and polarized views): (A) Broomcorn millet (*P. miliaceum*). (B) Triticeae. (C) Job's tears (*C. lacryma-jobi*). (D) Snake gourd root (*T. kirilowii*). (E) Yam (*Dioscorea* sp.). (F) Lily (*Lilium* sp.). (G) Bilobate. (H) Cross. (I) Rondel. (J)  $\eta$ -shaped phytoliths, consistent with broomcorn millet. (K) Dendritic epidermal phytoliths, consistent with barley (*H. vulgare*). (Scale bars: 10  $\mu$ m in A, H, and I; 20  $\mu$ m in B–G; 50  $\mu$ m in J and K.)



**Fig. 4.** Damaged starch grains from Mijiaya vessels and brewing experiments. (A) Mijiaya starch grains showing pitting and channeling. (B) A Mijiaya starch grain showing swollen, folded, and distorted characteristics. (C) Fermented broomcorn millet (*P. miliaceum*) starch grains from the brewing experiment using broomcorn millet and barley (*H. vulgare*). (D) A fermented gelatinized starch grain from the brewing experiment using broomcorn millet and barley. (Scale bars: 10  $\mu\text{m}$  in A and C; 20  $\mu\text{m}$  in B and D.)

subsistence in the Central Plain (29, 33). The microbotanical remains of barley at Mijiaya account for the earliest occurrence of this crop in China.

It is possible that the few rare finds of barley in the Central Plain during the Bronze Age indicate their earlier introduction as rare, exotic food. The Mijiaya farmers probably obtained small quantities of barley grains through exchange or cultivated the plant along with other cereals. We suggest that barley was initially introduced to the Central Plain as an ingredient for alcohol production rather than for subsistence. Because to our knowledge this is the first study that applies morphometric analysis to the dendritic phytoliths from China, future research with more comprehensive phytolith data from other Neolithic contexts is needed to test our hypothesis.

The practice of beer brewing is likely to have been associated with the increased social complexity in the Central Plain during the fourth millennium BC. The late Yangshao period in the Wei

River region was characterized by hierarchically organized settlement patterns, interpolity competitions, construction of large public architectures at regional centers, and ritual feasting likely organized by elite individuals and involving alcohol consumption (34) (*SI Text*). Like other alcoholic beverages, beer is one of the most widely used and versatile drugs in the world (35), and it has been used for negotiating different kinds of social relationships. The coincidence of beer production with other lines of material evidence suggests that competitive feasting was actively developing. The production and consumption of Yangshao beer may have contributed to the emergence of hierarchical societies in the Central Plain, the region known as “the cradle of Chinese civilization.”

## Materials and Methods

**Residue Extraction Methods Summary.** Chemical samples and two control samples (1, 3) were obtained by scraping off the sediments from the pottery surfaces with clean blades. Other residue samples were extracted by using an ultrasound bath or an ultrasound toothbrush. Starch and phytolith samples were floated from the residues using the heavy liquid sodium polytungstate at a specific gravity of 2.35. Extractions obtained from the residue samples were mounted in 50% (vol/vol) glycerol and 50% (vol/vol) distilled water on glass slides and scanned under a Zeiss Axio Scope A1 fitted with polarizing filters and differential interference contrast (DIC) optics, at 200 $\times$  and 400 $\times$  for both starches and phytoliths. Images were taken using a Zeiss AxioCam Hrc3 digital camera and Zeiss Axiovision software v4.8. See *SI Materials and Methods* for details.

**Determination of Oxalate Using IC.** Residue samples from Funnel 1, Pot 3, and Pot 5 were analyzed by a Dionex ICS 5000 with a conductivity detector, in Zhejiang Research Institute of Chemical Industry. The columns used were an Ion Pac-AS 11-HC Analytical (250  $\times$  4 mm I.D.) and an Ion Pac AG11-HC guard column (40  $\times$  4 mm I.D.) with an anion ASRS suppressor, operated at 20  $^{\circ}\text{C}$ . The eluent was 20 mM KOH and the flow rate was 1.5 mL/min; the injection loop was 25  $\mu\text{L}$ . Each residue sample produced two experimental samples. Each experimental sample (0.03 g) was dissolved in 3 mL nitric acid and diluted with 50 mL distilled water. Standard solutions were made from solutions of sodium oxalate in a concentration range between 0.0005 and 0.002 mg/mL. The calibration curve was established by linear regression analysis of peak height vs. added concentration of oxalate. The detection limit for oxalate under the given conditions is 0.036%. Control sample 4 was analyzed by a Dionex DX-500 IC with a conductivity detector, in the Environmental Measurements Facility at Stanford University. The eluent was 20 mM NaOH and the flow rate was 1 mL/min. Standardized solutions were made from solutions of oxalic acid in a concentration range between 0.1 and 10 mg/mL. Other laboratory conditions were the same as those used for the three residue samples.

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**Table 2.** Counts of phytolith types from vessels

Phytolith types	Taxonomic association	Funnel										Total	Control sample 1	Control sample 2	Control sample 3
		Funnel 1	Funnel 2	Pot 1	Pot 2	Pot 3	Pot 4	Pot 5	Pot 6	Pot 7					
$\eta$ -Type epidermal sheet element	( <i>P. miliaceum</i> )	4	3	0	3	1	3	5	0	6	25	2	0	0	
Cross	( <i>Panicoideae</i> )	37	23	26	81	32	63	52	45	35	394	0	2	0	
Bilobate	( <i>Panicoideae</i> )	49	18	16	62	26	24	50	22	15	282	0	2	0	
Polylobate	( <i>Panicoideae</i> )	3	2	2	14	2	14	1	5	1	44	0	1	0	
Articulated dendritic	( <i>Triticeae</i> )	2	11	0	76	33	24	27	4	0	177	0	0	0	
Undulate trapezoid	( <i>Pooideae</i> )	4	4	0	2	7	4	3	3	0	27	0	0	0	
Epidermal sheet element	( <i>Poaceae</i> )	0	14	4	12	12	12	11	6	11	82	4	0	3	
Bulliform	( <i>Poaceae</i> )	4	3	5	0	1	3	2	3	0	21	0	0	0	
Rondel	( <i>Poaceae</i> )	14	2	4	4	2	4	6	1	3	40	0	1	0	
Total		117	80	57	254	116	151	157	89	71	1,092	6	6	3	

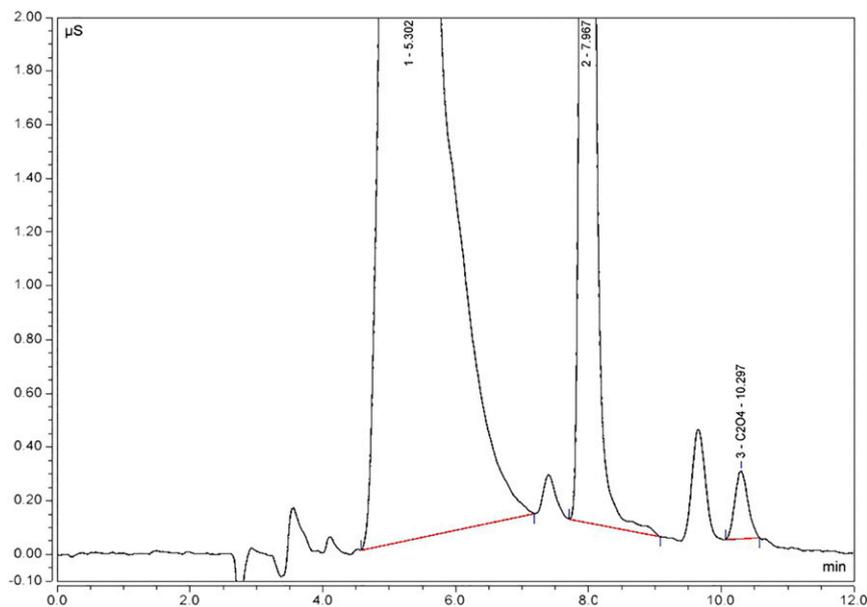


Fig. 5. IC of residues from Funnel 1, showing the presence of oxalate.

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