Technology and the Perfumer

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We have all heard stories about, and some of us remember the advent of the gas chromatograph. In those early days, the GC was often met with suspicion. To some its very existence was intimidating. In our insecurity we were sure that our art and our jobs would be gone with the wind! But, perhaps it wasn't just the GC, perhaps it was any number of technical innovations. Maybe we just thought that science was infringing a bit too much into an artistic area.

Today, however, we are faced with perfuming the myriad of products which flow from the minds of creative marketing. We now view technology as a God-send, a collaborator, a friend in need and sometimes a scapegoat.

Of all art forms, and I speak of perfumery as an art form, perfumery is one of the most technically oriented, an artistic extension of pharmacy perhaps. My father having been a pharmacist, I remember fondly the compounding rituals and the many fragrant materials that were used to make the various prescriptions more palatable or more fragrant in order to cover some God-awful "unguentum."

In any event, perfumers today are involved in many aspects of technology. Maybe they do not carry out the technical operations but should know when it is necessary to call on these vital tools to solve a particular problem. Nearly every fragrance brief we encounter from fine fragrances to reactive functional products gets us involved, whether we know it or not, in a good deal of technology.

In the work-a-day world of the perfumer probably the most often encountered technologies will be the gas chromatograph, physical/chemical considerations (i.e., pH, color and reactive bases) and most likely the isolation of fragrant materials from natural or synthetic mixtures. It is this last technological aid that I would like to focus on. We are concerned here with obtaining the fragrant oil in an appropriate form so that these analyses can be carried out successfully.

We may isolate fragrant material from natural sources for such reasons as the creation of essential oil replacements or to deal with quality control problems. At Givaudan we have a sophisticated program for the creation of natural product replacements, some of which are sold and many others which are used captively throughout the Givaudan group.

We isolate the perfume oil from synthetic

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mixtures such as soaps, shampoos or antiperspirants for the purpose of solving our customers' problems. For example, the headspace surrounding a customer's product may be studied in order to determine why fragrance is being lost through the packaging or what materials are involved in the interaction between fragrance and packaging material. Where fragrances are created for the specific use in very reactive media such as peroxide and chlorine bleach, the interaction and stability of the perfume ingredients may be studied by isolating the fragrance and determining what materials have changed and how much.

Special quality control problems may be more easily studied by isolating ingredients and determining what component or components are causing the off-odor or discoloration.

The methods used for isolating materials may be divided into four techniques: direct analysis, headspace analysis, chromatography and solvent extraction.

Direct Analysis

By direct analysis we mean that the fragrance oil need not be isolated as such before separation of components and identification. If the base is sufficiently volatile it may be injected directly into the GC for olfactory analysis, GC/MS or trapping-out. Also, I include here distillation. This technique lends itself well to direct analysis, and we have the luxury of working with larger amounts of materials. Natural oils, perfume oils or volatile bases containing perfume may be directly distilled in order to separate their components by boiling range and then followed up with an appropriate analysis. Since there are larger quantities involved here, there is a better chance for the trapping-out of individual components for further chemical analysis and identification.

Headspace Analysis

Headspace analysis is the collection and concentration of the air surrounding a fragrant material in order to identify the molecules responsible for the odor. Of all the isolation methods, headspace analysis represents more of the real world as far as the experience of fragrance is concerned because we are dealing with the quantity and quality of the odor molecules actually arriving at the olfactory centers.

Chromatography

Under chromatography I include those chromatographic techniques other than simple gas chromatography: column chromatography, high pressure liquid chromatography (HPLC), and thin layer chromatography (TLC). These chromatographic techniques can deal more easily with the nonvolatile portions of a fragrance which in many cases can be critical to the detection and identification of the high boiling molecules in natural gums and resins. Incidentally, I have found that TLC is a very handy little tool that requires very little equipment and can be made operational at a fraction of the cost of more sophisticated chromatographic systems. Although TLC must be considered a rather coarse separation method as compared to GC, what can be obtained are interesting and useful patterns that can help determine the presence of certain gums, resins, and absolutes. Usually the components are separated as narrow bands and are made visible by use of chemical sprays which produce different colors in specific patterns. For instance patchouli has a pattern of bright orange bands, oakmoss produces bright green bands. So this combination of color and pattern may be used as an identifying technique.

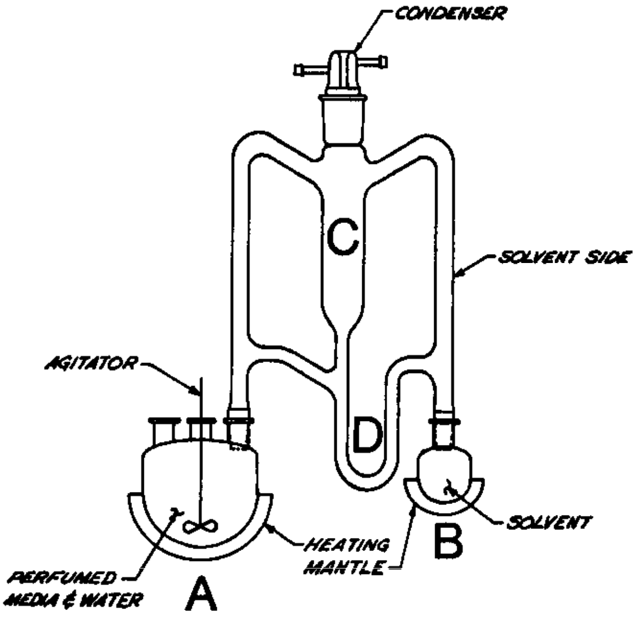

Figure 1

Solvent Extraction

In solvent extraction the perfume oil is usually separated in varying degrees of efficiency from some vehicle wherein the fragrance functions. This technique can range in complexity from shaking up a perfumed base in a test tube with some solvent, to rather sophisticated, controlled, quantitative extractions using complicated equipment.

Fragrant oils are complex mixtures of aroma chemicals, essential oils, gums and resins. If we are speaking of the perfume in a household product or cosmetic product, the picture becomes much more complicated with emulsifiers, clarifiers, thickening agents, solubilizers, surfactants, solvents and many other materials which make up the finished product. In addition the complex perfume oil is only present from say 0.05% to 1.5%. The analytical chemist, therefore, has a formidable separation and analytical challenge.

But, not to worry! Chemistry is on our side and in many cases we are saved by polarity and solubility. It turns out that our relatively non-polar fragrance is more soluble in our extracting solvents than the salts, acids and higher alcohols and other functional materials. However the base components may contain impurities which are often present in amounts equal to or larger than the amounts of fragrance and end up being extracted with the fragrance.

Some of the isolation techniques available include simple separatory funnel techniques, continuous liquid/liquid, Soxhlet and countercurrent extraction methods. Depending on the nature of the perfumed base, all of these methods have inherent problems, i.e., emulsions, foaming and low recovery. These problems led us to search for a method of extraction that would yield an extract representative of the composition of a perfume of unknown composition and in a state suitable for analysis.

In 1965, Likens and Nickerson reported in the *Journal of Chromatography* the use of a continuous steam/solvent extractor to isolate the volatiles present in hops.[1]

Figure 1 shows the original Likens design setup for extraction. Flask (A) contains water and the material to be extracted adjusted to a pH of 7.0. Flask (B) contains an appropriate solvent. The material in both flasks are then brought to reflux. Steam distillate and solvent vapor condense at (C) and extraction occurs in the solvent interface area (D). The aqueous phase is returned to flask (A) and the solvent containing extracted material to flask (B). Figure 1 is set up for the use of heavier than water solvent extraction. If lighter than water solvents are used, flasks (A) and (B) are reversed.

Early extractions using this method were very promising but it was soon discovered that this design was not capable of quantitative extractions. In addition, the extracts obtained contained more base ingredients than fragrance materials. Also, fragrance materials which were known to be present prior to extraction were not

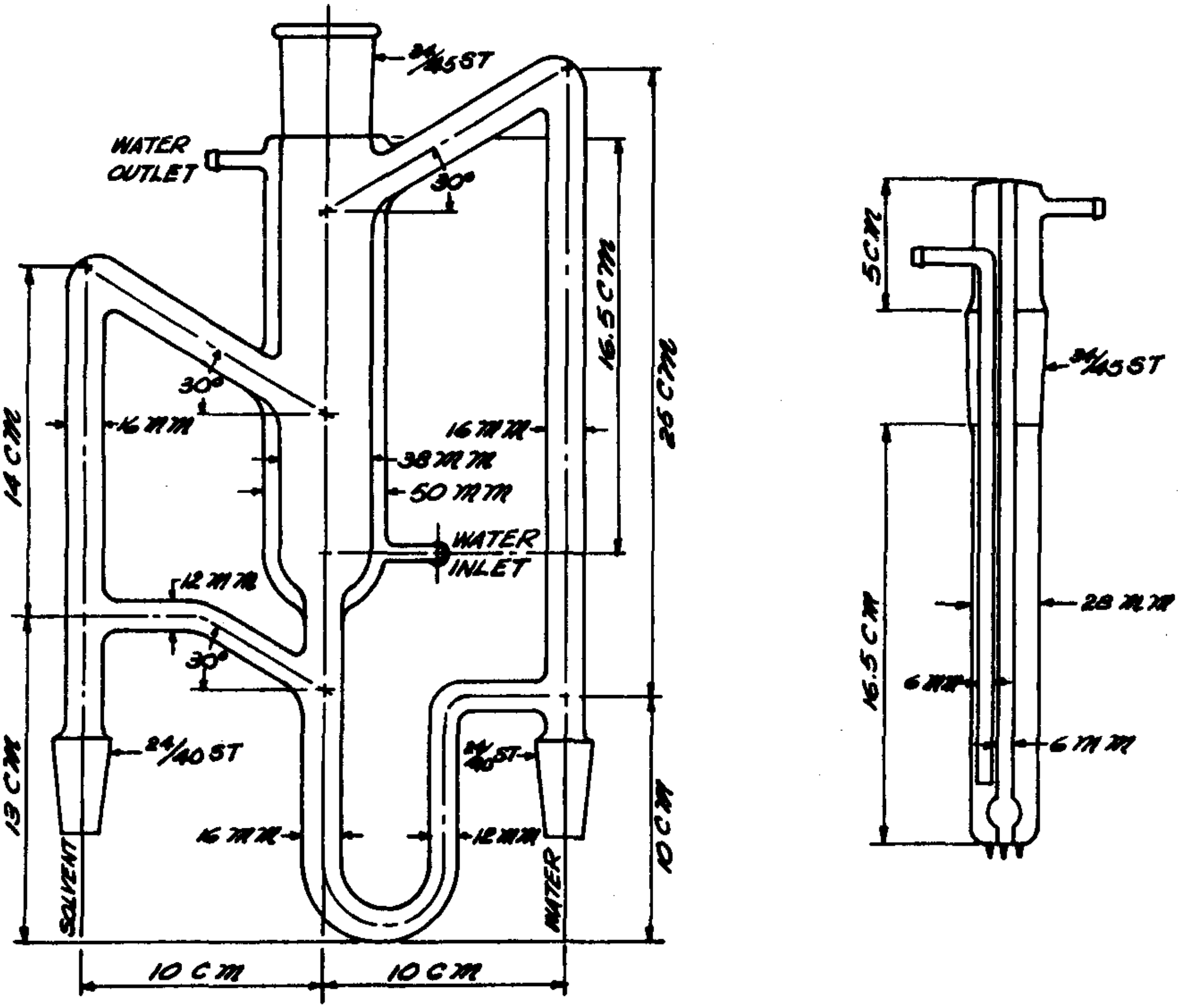

Figure 2

present in the extract. For example, cinnamic alcohol was found to be difficult to extract quantitatively and for this reason was used as a standard to determine the efficiency of the extractions.

Theoretically, quantitative, continuous extraction of a steam distillate should be possible. Therefore, it was assumed that the original extractor design was wrong for our purposes. A study of this extractor revealed several reasons for poor extraction:

- Poor boil-up due to insufficient condenser area
- Small solvent interface area providing inefficient extraction.

A program was then undertaken to modify the original Liken's extractor. A number of designs were tried. In the end two were finally fabricated which contained all the modifications which allowed an improvement in the efficiency of the extraction of cinnamic alcohol.

Figure 2 shows an extractor designed for lighter than water solvents such as pentane or diethyl ether. This extractor has the entry points of the water and solvent return tubes positioned at such a distance as to achieve maximum interface area. Here too the diameter of the interface was increased which also helped increase the extraction capacity. The installation of an outside condenser doubled the condenser area and allowed a higher boil-up rate than that found in the original extractor.

Figure 3 shows a similar extractor which was designed for heavier than water solvents such as methylene chloride, Freon 112, or carbon tetrachloride. This extractor as well as the preceding one were found to be capable of nearly quantitative extractions of cinnamic alcohol in a rea-

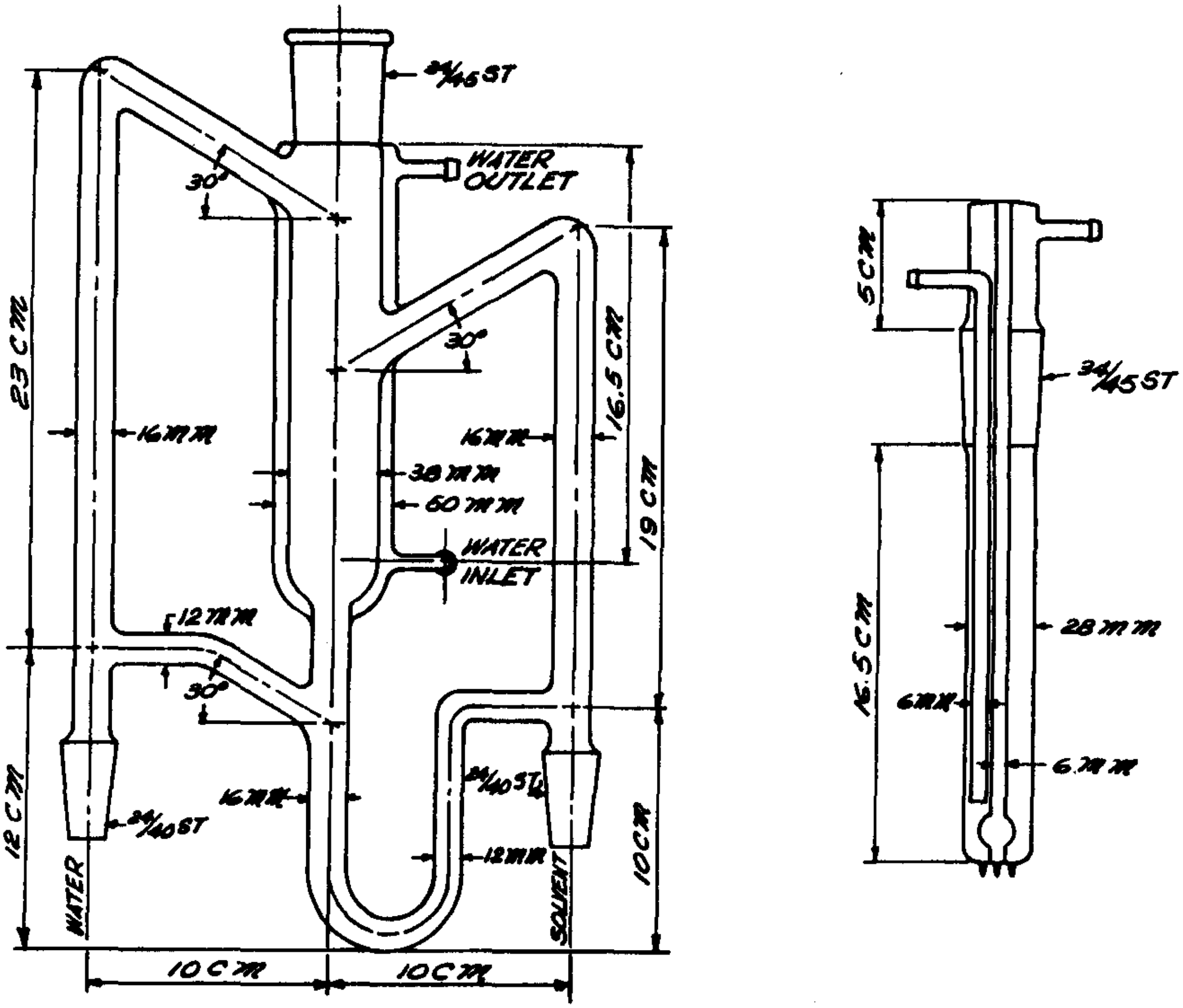

Figure 3

Table I. Cinnamic Alcohol Recovery

Time (Hours)	Ethyl Ether Likens	Ethyl Ether New Extractor	Methylene Chloride Likens	Methylene Chloride New Extractor
4	19	23	40	44
7	19-21	40	48	86
24	30	100	60	100

sonable period of time (approximately 24 hours.

Table I shows the results obtained with both extractors compared with the original Liken's extractor. As you can see the new design gives much better results than the original extractor.

Now for two practical examples. First, a fragrance of known composition was incorporated into a soap bar at 1%. The scented bar was grated and 100 g placed into a flask containing 1 liter of water. This mixture was neutralized to a pH of 7 and then extracted with 50 ml of methylene chloride for 24 hours. Prior to concentration of the solvent the methylene chloride extract was washed with a saturated sodium bicarbonate solution to remove volatile fatty acids present in the soap base. Table II shows the original formulation and the results of the extraction.

A similar operation was used for the analysis of a perfumed powdered laundry detergent. In this case however, analysis of the concentrated extract showed that it contained from 90%-95% dodecylbenzene (DDB) and only 5%-10% fragrance material. It turned out that the detergent base itself contained from 0.5% to 1% DDB resulting from incomplete sulfonation during its manufacture. To remove the DDB, the extract was subjected to column chromatography on silica gel. Concentration of the extract gave an oil

Table II. Composition of Standard Perfume Oil Obtained by Extraction

	Standard	7 Hrs.	24 Hrs.	48 Hrs.
Linalool	22.0	34.7	24.0	23.0
Benzyl acetate	13.8	19.5	14.0	13.0
Terpineol	2.1	3.1	2.4	1.9
Cinnamic alcohol	14.7	4.0	9.6	12.4
Cyclamen aldehyde	4.8	6.7	5.1	4.7
Amyl cinnamic aldehyde	16.8	15.5	18.5	17.1
Phenyl ethyl alcohol	12.3	7.5	13.0	12.9
Phenyl ethyl phenyl acetate	4.2	0.7	1.9	2.4
Musk tibetene	2.9	1.2	2.9	3.1
Perfume oil-weight		0.6152	0.9593	1.0915
Fatty acid weight		0.2707	1.1200	2.4345
Total extract weight		.8859	2.0793	3.5260

Table III. Analysis of a Standard Laundry Detergent Extract

Components	Before	After
Dihydrolinalool	0.5	0.4
Linalool	2.7	2.5
1-Terpineol	0.3	0.5
Cedrene	1.4	0.1
Elemene	2.3	2.3
Thujopsene	1.0	0.0
Terpineol	15.2	15.6
Citronellol	13.1	13.6
Geranial/neral	3.2	3.3
Phenyl ethyl alcohol	14.5	14.1
Cyclamen aldehyde	11.9	13.5
Anisic aldehyde	2.0	2.6
Lilial	7.7	8.4
Elemol	1.1	1.4
Cedrol	0.6	0.7
Heliotropin	3.0	3.1
Amyl cinnamic aldehyde	6.0	6.9
Dep	0.5	0.6
Coumarin	5.4	2.8
Musk xylol	2.2	2.4
Musk ambrette	1.3	1.4

suitable for analysis. The fragrance composition and extraction results are shown in Table III.

By using the modified Liken's extractor we can be reasonably certain that the composition of our extraction of unknown mixtures is fairly accurate. As you can see however, from the last example, solvent extractions are not always a simple technique. At times additional procedures are necessary to remove unwanted base components. There are no general rules; each extraction must be judged separately. Column chromatography as in our last example is an effective method. Various freezing techniques have also proved successful.

Today technology is advancing at a tremendous rate. There are not only great advances in instrumentation, chemistry and physics that we are able to apply to our practice of perfumery but we must not forget computer science. I don't mean the financial, materials management and research uses. For the most part all of us have computer generated cost books or computer terminals which give us up-to-date cost data and availability. I do mean the perfumer's own personal computer which can be used for keeping track of experiments or performing complicated formula manipulations. It is amazing what can be done with VisiCalc® and other spread sheet programs. Formulae may be stored, calculated, moved, merged and manipulated. Various word processing and file management programs can store ideas, references to fragrance types, odor data, stability and suitability of use data.

Why not a program that will take a fine fragrance formula, manipulate it, drawing on cost and stability files to generate a basic formula suitable for use in soap, detergent or antiperspirant? What a time saver to the perfumer to be able to do a cost reduction or revision for stability by merely editing the formula on the TV monitor. It may then be printed out so that it can be compounded and at the same time saved and catalogued for future reference, making a future job easier. The possibilities are endless. The perfumer must be allowed to give 100% of experience and creativity. The computer should do the filing, the remembering, the sorting.

As we rush headlong toward the twenty-first century, perfumery must keep up with technology to the extent that we become conscious of what new innovations are available to us. We must question, search, be aware. Our technical people should regularly keep us informed as to any new methods and ideas which might give us that competitive edge.

Perfumers, therefore, armed with the support and the understanding of science and technology may more confidently serve their customers and their art.

Acknowledgement

I would like to thank take this opportunity to thank Mr. Ken Purzycki, one of our Senior Research Chemists, who was responsible for modifying the Likens extractor.[2]

References

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