

## Product Review:

# Choosing Benchtop pH Meters

When shopping for a benchtop pH meter, it's the details that really count.

Curtis Phillips



Beckman Coulter 500 series benchtop pH meter

PHOTO COURTESY OF BECKMAN COULTER

A pH METER IS ONE of the first pieces of laboratory equipment that a winery lab should acquire. It is needed for many of the routine analyses that one should be running on every lot of must and wine in the winery. I do not advocate “wine-making by the numbers,” but one cannot even make reasonable SO<sub>2</sub> additions without knowing the must or wine pH beforehand.

As the name suggests, a pH meter measures pH. This is obviously handy for directly measuring juice and wine pH. However, there are other important and routine analyses that require a pH meter.

There are several designs of pH meters, ranging from very inexpensive all-in-one pen-type pH meters to ruggedized portable pH meters to benchtop pH meters. Other than the direct measurement of pH, most of the routine analyses requiring a pH meter involve titrations. While one could use a pen-type or portable pH meter for pretty much any titration, I find that their designs can be cumbersome while also dealing with a buret full of titer. Mainly the upper end of the pen-type meters gets in the way of the buret. Also, some pen-type meters don't display the pH continuously. The problem with titrating using a portable pH meter is really ergonomic. They are designed to be held in the hand rather than sit on a bench. For this reason, this article will focus on benchtop pH meters rather than their more portable brethren.

### TYPICAL USES

Three routine analyses require the use of a pH meter: pH, Titratable Acidity (TA) and Volatile Acidity (VA). In addition to directly measuring pH and using the meter for titration measurements like those for TA and VA, a pH meter is needed for standardizing acid and base standard solutions like the 0.01N NaOH standard used for determining SO<sub>2</sub> by aeration-oxidation.

### Routine Analyses

Strictly speaking, one doesn't really need a pH meter for acid-base titrations like TA and VA. One could titrate using phenolphthalein as an indicator. The endpoint for phenolphthalein is also pH 8.2, and a skilled technician can titrate to the indicator faster than most pH meters can lock in a measurement. Despite this, I'd much rather titrate using a pH meter. For one thing, the phenolphthalein endpoint can be hard to see in red wines. It's also fairly easy to overshoot the phenolphthalein endpoint.

### Other Uses

In addition to the measurement of pH and TA, a pH meter is needed for the standardization or normalization of acid or base titrants like the 0.01N NaOH titer (a titer is what's in the buret for the titration) used in the determination of SO<sub>2</sub> by aeration-oxidation.

These meters can be used to measure other ions as well. Ion Specific

week. A pH meter is needed for determining pH and TA (see Test Strips and Indicators sidebar).

Free SO<sub>2</sub> can be determined by the Ripper method, which is quick and doesn't require much additional glassware. It has been my experience, unfortunately, that small winery labs often get inaccurate results from the Ripper assay for free SO<sub>2</sub>. I suspect this is because the endpoint is a bit slow to form, which makes it easy to either overshoot the endpoint by titrating too fast or by freeing bound SO<sub>2</sub> by titrating too slowly.

An alternate method for determining free SO<sub>2</sub> is to use the Aeration-Oxidation (AO) assay. This method is slower and requires a little more glassware than the Ripper method, but I think it's an easier and more accurate method for determining SO<sub>2</sub> in a small winery lab. The AO assay uses 0.01N NaOH as a titer. The NaOH needs to be standardized every day by back titrating, using a pH meter or phenolphthalein indicator with HCl.

### Moderate Number of Wines

As the size of the winery grows, it should be possible to include at least a few tests in the more routine weekly analyses. In particular, I would add VA and total SO<sub>2</sub> analyses to the list above. Like TA and free SO<sub>2</sub>, one should use a pH meter for both—directly for acid-base titration in the case of VA and indirectly for standardization of the 0.01N NaOH for the total SO<sub>2</sub>.

Electrodes (aka Ion Selective Electrodes, or ISE) are more widely used for water analysis, but many larger wineries check potassium levels in juice using potassium ISEs.

### BROAD USAGE SCENARIOS

In terms of lab work, a wine lot is a wine lot. It doesn't matter if it's 50 gallons or 50,000 gallons; it's the same amount of work. It also doesn't really matter if all the individual lots are combined into relatively few finished wines. It's the number of wine lots that determines the amount of lab work.

Many routine juice or wine analyses require a pH meter, at least indirectly.

### Small Wineries

One of the main problems for small wineries or wineries producing few individual wine lots is that they need data just as good as the large wineries do, but they often lack the financial wherewithal to have a fully equipped winery laboratory. All the same, at an absolute minimum, every winery should be checking the pH, TA and free SO<sub>2</sub> on every wine in the cellar every

Benchtop pH Meters Manufacturers				
Company	Location	Phone	Web Address	Brands
Beckman Coulter	Fullerton, CA	800-742-2345	www.beckmancoulter.com	Beckman
Cole-Parmer	Vernon Hills, IL	800-323-4340	www.coleparmer.com	Cole-Parmer
Fisher Scientific	Pittsburgh, PA	412-490-8300	www.fishersci.com	Fisher Scientific
Hanna Instruments	N. Highlands, CA	916-349-7676	www.hannainst.com	Hanna Instruments
Metrohm USA Inc	Riverview, FL	800-727-6768	www.metrohm.com	Metrohm
Mettler Toledo	Columbus, OH	800-METTLER	us.mt.com	Mettler Toledo
Milwaukee Instruments	Rocky Mount, NC	252-443-3630	www.milwaukeeesters.com	Milwaukee Instruments
Oakton Instruments	Vernon Hills, IL	888-462-5866	www.4oakton.com	Oakton
Radiometer Analytical	France	+33 0 4 78 03 38 38	www.radiometer-analytical.com	Radiometer Analytical
Thermo Fisher Scientific	Waltham, MA	781-622-1000	www.thermo.com	Orion
VWR	Brisbane, CA	415-330-4230	www.vwrsp.com	VWR sympHony

**Large Wineries**

Large wineries have the problem of getting swamped by having a large number of samples to analyze. When a winery gets to the point that it's making much more than 100 or 200 individual wine lots, it's really time to get an auto titrator which, due to its additional complexity, is really a different class of equipment even though it has a pH at its core.

**IMPORTANT ATTRIBUTES**

A pH meter should be almost as straightforward as a screwdriver. It should just work. If it takes too much fiddling and futzing to calibrate, the meter isn't worth owning.

**Dedicated vs. Multi-function**

Simple pH meters can be used for acid base titrations and to measure pH. Multi-function meters can be used with different electrodes to measure other

things including specific ions, dissolved oxygen (DO), conductivity, resistivity, salinity and redox potential.

Many of these features are more important to other industries, especially water treatment; however, these days most wineries should be measuring dissolved oxygen as part of their bottling line quality control regime.

**Range of pH Measured**

The pH range of wine is pretty small; we rarely have wines with a pH lower than pH 3 or higher than pH 4. Even when measuring TA we just go up to a little more than pH 8.2, the pH equilibrium point for tartaric acid. A typical pH meter with the range of pH 0.00 to pH 14.00 should be more than adequate.

**Accuracy**

For day-to-day pH measurements, a winery production lab probably only

needs to measure pH to the nearest ±0.01 pH. All the benchtop meters listed in this article meet this minimum requirement. However, as a rule I prefer to have instruments that are more accurate than I am. For this reason, I prefer pH meters that are accurate to the nearest ±0.001 pH.

**Response**

The response of a meter is a description of the time it takes for the meter to measure a single sample. This is greatly influenced by the pH electrode used, but the meter itself is also important.

**Temperature Compensation**

The response of a pH electrode depends upon the temperature of the solution measured. This is because a pH meter really measures the activity of the hydrogen ions (H+) in the solution rather than directly measuring the H+ concentration. The activity

increases as temperature increases and decreases as temperature decreases. The drift due to temperature can be calculated, but I view having a temperature-compensated pH electrode as an absolute requirement. It's just not worth the hassle of not having one.

**Connectivity**

A pH meter may or may not have the ability to be connected to a printer and/or a computer as a way of recording individual measurements. While I think such connectivity is absolutely essential in automated equipment (like an autotitrator, for example), in my experience I have found that the usefulness of either depends greatly upon the way one approaches lab work. Unless one is going to be measuring a large number of samples at the same time, babysitting a computer-connected pH meter can be slower and more cumbersome than merely recording pH measurements and titrations into a lab book for later data entry.

**HOW AND WHAT TO BUY**

There are a large number of pH meter manufacturers. Almost all of the benchtop pH meters on the market can be used in a winery lab. Winemakers should be mindful that most of the least expensive and portable meters available were designed to measure the pH of water rather than juice. This means that one should expect to replace the pH electrode much more

Benchtop pH Meters Manufacturers										
Brand	Model	pH Range	Accuracy	Calibration	Temp Compensation	mV	Dissolved Oxygen	Connectivity	Price*	
Beckman Coulter	Beckman Coulter	Φ 350	0.00 to 16.00	±0.01	1 to 5 points	±0.5°	±0.2 mV	N/A	RS232	\$695.00
		Φ 510	-2.00 to 19.99	±0.01	1 to 5 points	±0.5°	N/A	N/A	USB	\$800.00
		Φ 570	-2.00 to 19.99	±0.01	1 to 5 points	±0.5°	*	*	USB	\$2,300.00
Hanna Instruments	Hanna	HI 222	-2.00 to 16.00	±0.01	1 or 2 points	±0.5°	*		RS232	\$525.00
		HI 2210	-2.00 to 16.00	±0.01	1 or 2 points	±0.5°	*		RS232	\$330.00
Metrohm USA	Metrohm	Metrohm 780	0.00 to 14.00	±0.001	1, 2 or 3 points	±0.1°	±0.1 mV		IrDA (printer only)	N/A
		Metrohm 867	0.00 to 14.00	±0.001	1 to 5 points	±0.1°	±0.1 mV		USB	N/A
Mettler Toledo	Mettler Toledo	S20 SevenEasy	0.00 to 14.00	±0.01	1, 2 or 3 points	±0.5°	*		RS232	\$685.00
Milwaukee Instruments	Milwaukee Ins.	Mi150	-2.00 to 16.00	±0.01	1 or 2 points	±0.04°	N/A	N/A		\$250.00
Oakton Instruments	Oakton	pH 500	0.00 to 14.00	±0.01	1, 2 or 3 points	±0.5°	±0.2 mV			\$600.00
Radiometer Analytical	Radiometer Ana.	ION450	-9.000 to 23.000	±0.001	1 to 9 points	±0.1°	±0.1 mV		RS232	\$2,652.00
		PHM240	-9.000 to 23.000	±0.001	1 to 9 points	±0.1°	±0.1 mV	*	RS232	\$500.00
Thermo Scientific	Cole-Parmer	Cole-Parmer	0.00 to 14.00	±0.01	Manual	Manual	±10 mV	N/A	none	\$275.00
	Fisher Scientific	Accumet Basic 15	-1.99 to 19.99	±0.01	1 to 5 points	±0.5°	*		none	\$910.00
		Accumet Basic 15+	-1.99 to 19.99	±0.002	1 to 5 points	±0.5°	*		RS232	\$1,220.00
	Orion	2-Star	0.00 to 14.00	±0.002	1, 2 or 3 points	±0.1°	*	N/A	RS232	\$435.00
	3-Star Plus	-2.00 to 19.99	±0.01	1 to 5 points	±0.5°	*	*	USB	\$900.00	
VWR	VWR sympHony	SB70P	-2.00 to 19.999	±0.002		±0.1°	±0.1 mV	N/A	USB	\$600.00
		SB80PI	-2.00 to 19.999	±0.002		±0.1°	±0.1 mV	N/A	USB	\$1,000.00

\* Approximate prices only, actual prices may vary.

## What About Alternatives?

It might seem reasonable to ask if pH meters are the only way to measure pH. There are both more and less expensive ways to measure it.

### TEST STRIPS AND INDICATORS

Readers may remember the litmus test strips used to measure pH in swimming pools. Specialized versions of these strips like those from **Accuvin** ([www.accuvin.com](http://www.accuvin.com)) are extremely easy to use and are getting pretty accurate. In theory, one could forego purchasing a pH meter and use the strips for most of a winery's routine analysis. One should note that the cost of each test is about \$2. I recommend that a winery measure at least the pH, TA and free SO<sub>2</sub> of every wine lot every week. At this admittedly high rate of analysis, it only takes 7 to 10 wine lots in a given year for the test strips to cost more than a very nice pH meter.

The main limitation of test strips is that they only allow one to measure pH. One cannot use them for titrations. An indicator can also be used, however. A phenolphthalein indicator turns purple-red at pH 8.2, which is just the pH one needs. The endpoint is a bit more responsive than the average pH meter, which can save a bit of time. Despite this, I'm not a big fan of indicator-based titrations. For one thing, it can be hard to see a red endpoint in a red wine. My main gripe, however, is that indicator-based titration endpoints are too easily overshoot by lazy or inexperienced lab technicians. Not that a pH meter is idiot-proof, but at least it will tell you when you've used too much NaOH by displaying a pH well past the endpoint.

### WINE ANALYSIS IN A BOX

A couple of extremely interesting devices for winery laboratories have come onto the market in the last couple of years. **FOSS** introduced its OenoFoss last year at the Unified Wine and Grape Symposium. One could describe them as wine-labs-in-a-box. All appear to be designed to perform routine wine analyses. **Alpine Scientific** has entered this sector as well. It would seem reasonable to ask if one ought to forego getting a pH meter and get one of these all-in-one units instead. The problem is, even if these units could completely replace your pH meter, and I don't think they can or should, any winery lab that can afford the \$10,000 to \$20,000 that these units cost should be able to cough up another \$500 for a good pH meter. **wbm**

frequently than the manufacturer's literature indicates.

### Tight Budget Tips

A pH meter is fairly inexpensive, with the least expensive examples costing less than \$300. Since a winery production lab can make do with a pretty modest pH meter, one can get a no-frills benchtop meter for around \$200; indeed, one can also get a pen-type meter for under \$100. It is tempting to buy on price when the budget is tight.

There are two features that I would consider as absolute requirements even when money's tight. First off, I would never get a pH meter that didn't have automatic temperature compensation. This is not because I can't do the math; I can, and frankly, within a couple of degrees from 20°C it's not needed; but wine is rarely kept at that warm a temperature. My time is more valuable than the additional cost of the feature. The second feature I won't do without is three-point calibration.

### Moderate Production

If your winery is making more than 100 discrete lots of wine per year, getting a pH meter that does as much of the grunt work on its own is best so that the lab tech can spend his or her time more productively. At a minimum, one should invest in a pH meter that automatically recognizes standardization buffers and that outputs all its measurements to a PC rather than a printer.

This is also the point at which it becomes a good idea to get a pH meter that can do more than just measure pH.



PHOTO COURTESY OF BECKMAN COULTER

Dr. Arnold O. Beckman invented the pH meter in 1934, to help a friend in the citrus industry measure the pH of lemons. It was the first integrated, portable instrument that a person could buy off the shelf to measure the chemical properties of a variety of substances. The image shows the first production model, the Model G pH Meter. Nearly 28,000 were produced from early 1937 through 1969.

I used to think that it was more important to get a meter that works with an ion selective electrode (ISE) so that one can do potassium analysis, but these days I think it's more important to get a pH meter capable of measuring dissolved oxygen (DO).

### MANUFACTURER DESCRIPTIONS

There are a great many more brands of pH meters on the market than are represented here. However, these are the ones that predominate here.

### CONCLUSION

When shopping for a pH meter:

- Think in terms of number of samples (i.e., number of wine lots) rather than in terms of total production.
- Don't let parsimony get in the way of buying needed features like temperature compensation.
- Buying an mV, Ion and DO-capable meter greatly increases the flexibility of the instrument.
- If your lab isn't measuring dissolved oxygen, it ought to be. **wbm**

## Benchtop pH Meters

### Vendors

Company	Location	Phone	Web Address	Brands
American Tartaric	Windsor, CA	707-836-6840	<a href="http://www.americantartaric.com">www.americantartaric.com</a>	Hanna Instruments
Davis Instruments	Vernon Hills, IL	800-358-5525	<a href="http://www.davis.com">www.davis.com</a>	Hanna, Oakton, Thermo Scientific, Orion
Gusmer Enterprises	Fresno & Napa, CA	866-213-1131	<a href="http://www.gusmerwine.com">www.gusmerwine.com</a>	Mettler Toledo
GW Kent	Ypsilanti, MI	800-333-4288	<a href="http://wineryparts.com">wineryparts.com</a>	Hanna Instruments
Hach Company	Loveland, CO	970-669-3050	<a href="http://www.hach.com/ra">www.hach.com/ra</a>	Radiometer Analytical
TCW	Saint Helena, CA	707-963-9681	<a href="http://www.tcw-web.com">www.tcw-web.com</a>	Hanna Instruments
Vinquiry	Windsor, CA	707-838-6312	<a href="http://www.vinquiry.com">www.vinquiry.com</a>	Beckman-Coulter & Orion