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A SYSTEM FOR INTERNATIONAL EXCHANGE OF SAMPLES FOR TRACE ELEMENT ANALYSIS OF OCEAN WATER

BY

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ABSTRACT

The hazards inherent in sampling at sea for trace element analyses are discussed. It is proposed that a discussion be held at Helsinki in 1960 on:—

- (a) sampling for trace element analysis;
- (b) a system for international exchange of samples and for reciprocal control of methods for analysis of trace elements.

INTRODUCTION

For many of the elements present in the sea in trace amounts, it is difficult to glean from the literature any firm idea of the amounts truly present in the ocean (Goldberg, private communication; Richards, 1956¹). For some elements the reports from different analysts vary by several orders of magnitude. Elements taking part in the biological cycle have naturally a wide range of concentrations in the more accessible shallow waters, where they are often poorer than in the deep ocean reservoirs. Also, the deep Atlantic, due to its more vigorous vertical circulation, is often notably poorer than the deep Pacific.

In greater part, however, discrepancies arise from contamination, often gross, of the samples.

We need a measure of the mean content of trace elements and of trace organic constituents of the ocean. Such information cannot be had without sampling the deep oceans. We also need reliable measures of the way in which distribution varies from place to place or from time to time due to biochemical, physico-chemical, or geochemical processes. It is essential to be able to compare confidently the results of many analysts in many laboratories using

¹ F. A. Richards, 1956. On the state of our knowledge of trace elements in the ocean. *Geochim. Cosmochim. Acta*, 10: 241-243.

methods which, from the nature of the problem, do not admit of standardization at the present time.

It is practical to arrange a supply of "standard sea water" for determinations which are made in quantity and which satisfy other exacting requirements, as for determinations of chlorinity. Abundance of analyses and consequent cross checking enables us also to have reasonable confidence in figures for the distribution of phosphate, silicate, nitrite and oxygen. For all other trace constituents, the only practicable check seems to be through encouragement of an exchange of samples between analysts who have the means of collection at hand and who are aware of the need for accuracy.

Faults in Technique. Shortcomings of standard oceanographic apparatus and techniques for collecting samples at sea for trace analyses are:—

(a) Contamination of a sample by material from the sampling gear, which is often made from an alloy of copper, possibly electroplated. Copper and elements of its numerous alloys as well as elements used in electroplating or anodizing are ever-likely contaminants.

(b) Contamination of a sample by the patina which may accumulate on collecting and storage bottles or by organic coatings. Iron and elements which co-precipitate with ferric hydroxide may be introduced in this way.

(c) Contamination by rust from the steel wire which supports the bottle. Although iron and zinc are the most likely contaminants from this source, today many elements are alloyed into steel.

(d) Contamination from the bottle in which a sample may be stored, or loss by adsorption of constituents from the sample onto the surface of the container. Contamination varies with the nature of the bottle. Glass may be very treacherous, and although polythene seems to be ideal for short-time storage of samples intended for silicate analysis, it has not been established unreservedly that it is suitable for everything; not only is it permeable to water, but it seems liable to absorb or adsorb material from one sample and to give it back to later ones.

(e) Contamination from materials in rubber washers and stoppers. This has been given little thought. Antimony sulphide is used less often now than it used to be in compounding rubber, but the number of contaminants which may leach out of commercial vulcanized rubber was and remains legion. Neoprene should be considered.

(f) Contamination on board ship from the hands of the operators. At sea it is more difficult to keep the hands clean than in a shore laboratory. Rust and grease are the worst offenders when work has to be carried on from a small ship in poor weather.

(g) Contamination by smoke and ash from smoke-stacks, galley chimneys, or a lighted cigarette to windward, and from sewage and waste of all kinds discharged from the ship during sampling. Rarely are these hazards sufficiently appreciated.

(h) Presence or concentration of an element sought in or upon either living organisms or non-living detritus in the sampled water can hardly be called contamination, but it may cause annoying lack of agreement between replicate samples.

It will be appreciated that the standards maintained for the collection of samples for analyses of chlorinity and oxygen, though stringent, fall short of what should be demanded by a trace analyst. It is quite unreasonable for an analytical chemist to ask a physical oceanographer, pursuing other ends, to collect samples according to the exacting demands which the analyst ought to insist upon. Chemists must collect their own samples and must work together internationally to obtain and exchange samples of known history; furthermore, they must, in mutual interest, be prepared to undertake preliminary work at sea, such as filtration.

Necessary Advances. Steps to overcome these sources of error will differ according to the trace constituent under examination, *e. g.*, iron and copper behave quite differently as contaminants. In general, non-metallic gear should be used so far as possible for collecting samples for metal analyses. A number of laboratories have now constructed closing bottles in polythene. Although many will not have the resources to use a complete "hydrographic wire" made of nylon or terylene, an extension of 50 m or so of such material, to be worked below a steel wire at any depth, is possible.

For storage, the choice at present seems to rest between glass, polythene (polyethylene and now polypropylene) and other plastics. It would seem wise, if possible, to avoid spring stoppered, screw-stoppered, or ground-glass stoppered bottles. Ideally, glass bottles intended for storage of samples for analyses of trace elements should be made from sand, soda, lime, and maybe borax, of Analytical Reagent quality or better. A commercial firm, prepared to execute a trifling order to such a stringent specification, would be

hard to find. Is the need by chemical oceanographers sufficient for an approach to a glass industry research association (or similar body) to devise specifications and to manufacture a few gross bottles?

Again, is there a case for glass or polythene phials with narrow necks which, after filling, may be at once sealed on board with a blow-pipe flame? With canisters of Calor-gas or hydrogen, such a blow-pipe is practicable on any ship. Transport of such sealed samples by land, sea or air would then be easy and free from risk of contamination or leakage during transit.

Standard Stations. For work such as this the Plymouth Laboratory has established a standard station in the Bay of Biscay at Lat. $46^{\circ}30'$ N, Long. $8^{\circ}00'$ W, in 4710 m depth. Samples to the bottom have been drawn for a number of British Laboratories for precision analyses of chlorinity, oxygen, phosphate, total phosphorous, silicate, arsenic, rubidium, caesium, iron, copper, strontium, gallium, germanium, cadmium, gold, uranium and vitamin B₁₂; deuterium is being analysed in the United States. Eventually we shall have a considerable store of information for comparison with determinations elsewhere and with further information which will be collected at the same position in the future. We are prepared, within our resources and at our own convenience, to collect similar samples (not exceeding one litre, or five litres exceptionally) for analysts elsewhere. The recipients of such samples would be expected to bear the expense of bottles and transportation.

The conditions of a general expedition, with a tight programme of varied work and diverse interests, rarely encourage the sacrifice of time which sampling for trace analyses demands. In my opinion, it is better and much easier to obtain optimal conditions for sampling trace elements on a short economical excursion designed for this purpose alone and with a chemist in charge.

It seems that chemical oceanography would be best advanced by choosing carefully a few standard stations, widely spread over the world, where pioneer work would be concentrated and from which samples would be distributed on an exchange basis. Such stations, in depths preferably exceeding 4000 m, would be as close as convenient to laboratories devoted to chemical oceanography. Excursions to these stations would be in charge of analytical chemists who would have similar standards of accuracy and achievement and who will have learned to trust experienced colleagues operating

similar stations in other waters. Mutual confidence is essential. Not until methods had been well proved under the most favourable conditions would they be employed on general expeditions with varied programmes and severe competition for available time and gear.

Isolated analysts and geochemists interested in the sea should be encouraged to use such a tested service to obtain the samples they need. They could, with advantage, be encouraged to participate in order to learn for themselves how to overcome the difficulties normally encountered in trace element work.

International Co-operation. Many independent analysts, and others at small marine laboratories, may find themselves unable to provide suitable sample containers or to defray considerable carriage charges.

An international body seems necessary:—

- (a) To encourage oceanographic laboratories to collect samples for exchange according to the stringent standards of chemical cleanliness which are necessary.
- (b) To specify such standards and to concentrate efforts in skilled hands.
- (c) To encourage the design, manufacture and distribution of suitable sample containers.
- (d) To place analytical chemists and geochemists in need of samples in contact with those who can get them.
- (e) To obtain funds to defray costs of carriage and containers.
- (f) To arrange smooth passage through customs.
- (g) To arrange for re-use of containers on a "common-user" basis, as railway managements operate freight trucks. This would avoid the costly transport of numbers of "returned empties" about the world.

The Committee on Chemical Oceanography appointed by the International Association of Physical Oceanography at Toronto in September 1957, with myself as Chairman, is an international body which might consider undertaking this work.

Therefore it is proposed that a discussion should take place during the meeting of the International Association of Physical Oceanography at Helsinki in 1960, embracing the following subjects:—

"Sampling for trace element analysis" and "A system for international exchange of samples and for reciprocal control of methods for analysis of trace elements".

WAVE PATTERNS OFF SOUTHERN CALIFORNIA¹

By

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ABSTRACT

Mapping of wave trains during four flights over the ocean off southern California showed the consistent presence of a high 10-second swell from the westnorthwest, of one or two low 3- to 5-second swells from other westerly directions, and of local wind waves; occasionally a low 13-second swell from the west and southwest was also present. Islands reduce the height of swells but produce little discernable cross-swell in their lee. Maps of swells and wind waves provide information on the best courses to be followed by airplanes during ditching at sea; they may also aid in the interpretation of wave recordings at shore stations. The direction of most swells is such as to drive the sand of mainland beaches to the southeast in general, according with the known chief direction of accumulation of sand against artificial beach structures.

INTRODUCTION

Charts showing the direction of movement of ocean waves were made and used for navigational purposes by the Marshall Islanders until the end of the nineteenth century. Such charts were constructed of split palm stems arranged in a frame, on which were fixed shells to denote islands and short parallel sticks to represent swells. Examples of the charts and a summary description of them have been given by Emery, *et al.* (1954; 4, 5, pl. 1). Made by acute observers of nature, these charts represent a form of wave study that has not been investigated by modern man with his array of elaborate instruments. Instead, recent work on ocean waves has been directed mostly toward studies of refraction in local areas of shallow water (Munk and Traylor, 1947), of the spectrum of wave heights measured at shore stations (Munk, 1947) and computed from weather maps (Saur, *et al.*, 1947), and of the influence of waves on natural (Munk and Sargent, 1948) or artificial (Fleming and Bates, 1951) structures.

In order to learn whether an improvement might be made over Polynesian techniques and to determine the wave pattern existing

¹ Allan Hancock Foundation Contribution No. 230.

off southern California, the writer made wave observations aboard the University of Southern California's R/V *VELERO IV* during cruises that were set up mainly for other purposes. Azimuths of two or more sets of wave trains were noted both visually and on a radar scope. It was soon learned, however, that wind and wave conditions in this region vary too rapidly to permit mapping of waves during the several days that are required to cover the area by ship.

Observation from an airplane was obviously required. Through the interest of the Office of Naval Research, facilities were made available by Fleet Air Wing Fourteen, Naval Air Station, North Island, San Diego. Four flights were made at three-month intervals, on 15 October 1957, 16 January, 15 April, and 15 July 1958, using the Marlin (P5M) seaplane for three flights and the Neptune (P2V) amphibious plane for one. The high degree of visibility from the latter made it ideal for the work. Excellent co-operation was provided by administrative and flight personnel. Appreciation is also due D. S. Gorsline, R. L. Dunbar, E. S. Roth, and R. E. Stevenson, students of marine geology at University of Southern California, each of whom acted as recorder on one or more flights.

METHOD

Flight lines totalling 720 to 910 statute miles were covered in 4 to 6 hours; differences between the four flight plans came about because of military restrictions (imposed by Point Mugu Missile Test Center) and because of a desire on the second flight to follow a closely spaced grid. Positions were obtained by radar fixes at 15- to 30-minute intervals. Since flights had to be scheduled a week or two in advance, no selection of weather was possible; however, each flight happened to occur on a day of typical weather with northwesterly winds of 10 to 20 miles per hour in all of the region except near the northwestern corner of the survey, where winds were 20 to 30 miles per hour.

After some experimentation, an elevation of 2000 feet was selected as most suitable for identifying separate wave trains; observation at lower elevations caused some confusion by too great detail, and at much higher elevations trains of small waves tended to be overlooked. Owing to low clouds, the fourth flight was made at only 400 feet.

Observation was purely visual and was found to be clearest when

wave trains were viewed away from the sun at an angle of about 45° from their crest azimuth and at a downward angle of 15 to 45° . This angle of view permitted identification of waves by the alternation of dark and light stripes at the near and far sides of wave crests produced by differences in the ratio of light coming from within the water and reflected from its surface. Cross-checks on the direction of waves were made as frequently as practicable, usually at about 10-minute intervals, by viewing at the opposite side of the airplane.

In order to simplify the work, a wooden pelorus was mounted at the observation station with its fore and aft line parallel to the airplane's axis; the disk was turned until its indicated direction matched the airplane's true compass heading. Each of three moveable arms pivoted at the center of the disk was set as nearly parallel to wave crests as could be judged. The error of setting, as indicated by back sights and by comparison of results obtained on different flight legs, was usually less than 10° . During flight the observer attempted to keep the arms set at all times, reading off the settings at 1- or 2-minute intervals. These settings were noted by a recorder who also made frequent estimates of the period of waves in each train by timing the passage of waves beneath patches of foam, floating kelp, or gulls resting on the water. The position of each observation point was determined by interpolation between the less frequent radar position fixes.

About 50 photographs of waves were made during each flight with an aerial camera in order to check and illustrate typical patterns. Photography, however, was found to be a poor method for making the primary observations because of the small area included in each picture, the uncertainty of orientation and interpretation of the pictures, and the need of observation for several minutes before certain identification could be made of trains of smaller waves.

RESULTS

Maps of the wave patterns compiled after each of the four flights (Figs. 1 to 4) are similar in many respects. All show the predominant swell from the North Pacific storm area proceeding eastsoutheasterly throughout the area, with little directional control exerted by islands. Its period averaged about 10 seconds. One or two other swells, usually having 3- to 5-second periods and moving easterly

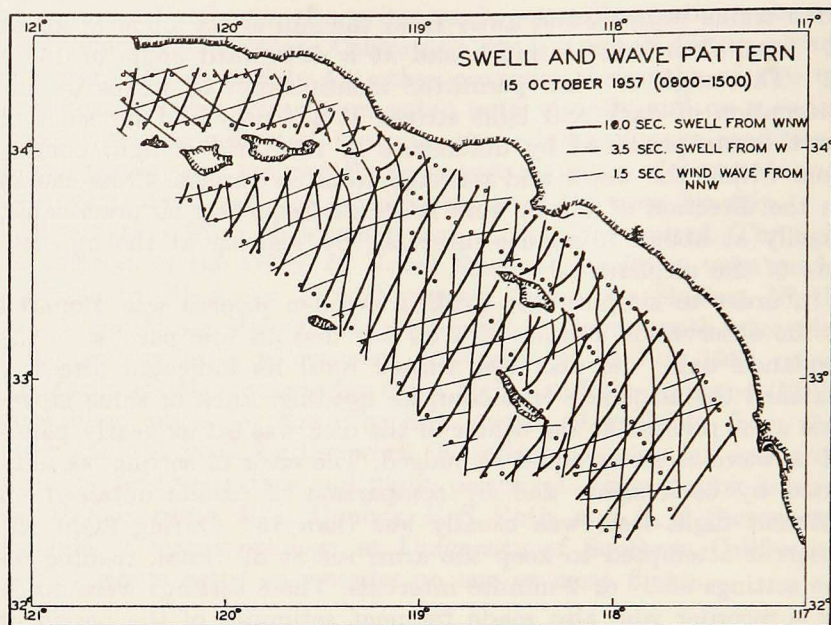


Figure 1. Survey of 15 October 1957. Flown aboard P5M at 1500 and 2000 feet. Circles show positions of observation points along flight lines. The spacing of swell and wind wave lines is arbitrary and carries no implication regarding wave lengths.

or northeasterly, probably originated from storms in the central Pacific Ocean. A long low swell, possibly from a storm center in the southern hemisphere, was detected in the southwestern part of the area during the July survey; and it may have been present in areas of low waves in the eastern part of the area during the April survey. Because of its length and lowness, it was easily obscured by accompanying shorter and higher swells. Each survey also showed the presence of a wind wave, usually of about 1.5-second period, moving southerly and following the typical wind stream lines of the region. Long narrow parallel streaks were observed to be perpendicular to the crests of wind waves in areas of high wind velocity near the northwestern part of the surveys. Both smaller swells and wind waves are influenced by islands, mostly in the form of gaps in the lee of islands.

Refraction by shallow water was noted only near the shores of the mainland and islands. Cross-swells in the lee of islands were

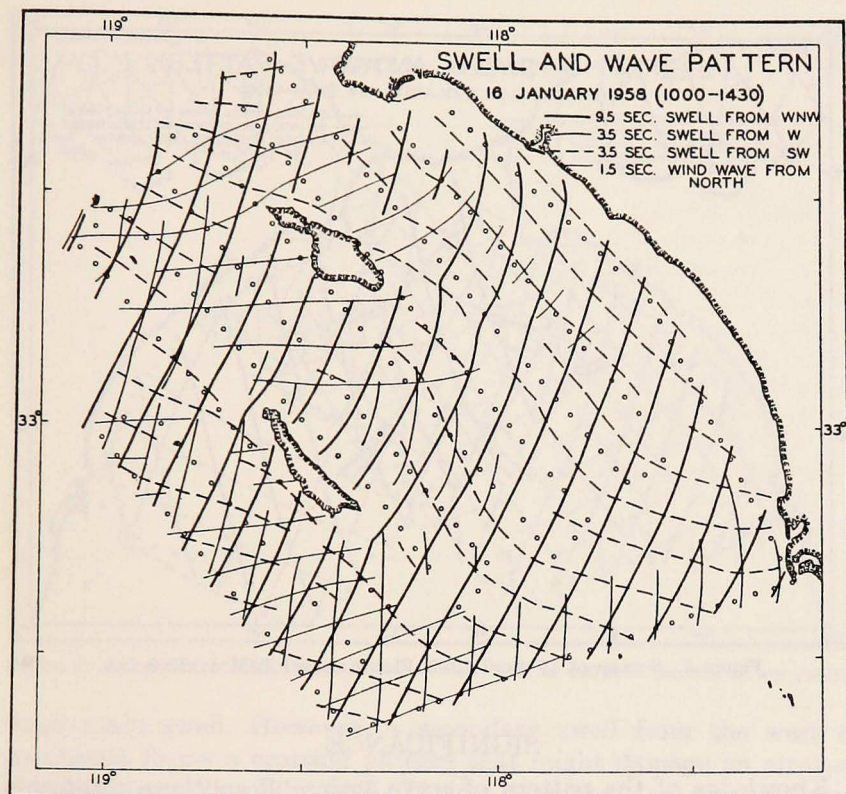


Figure 2. Survey of 16 January 1958 with a closely spaced grid. Flown aboard P2V at 2000 feet. Some uncertainty of the smaller swells and wind wave resulted from disturbances produced by naval vessels operating near the middle of the survey area.

not detectable over large areas. Reflection of waves was even less important. In these respects, the islands off southern California appear to have less effect on waves than do islands of the tropics. Perhaps the effects of the latter islands, as observed by the Marshall Islanders and others, result from the relative simplicity of wave patterns in the belts of trade winds compared with the complexity of patterns off southern California where they are developed by several separate storm centers and by local winds.

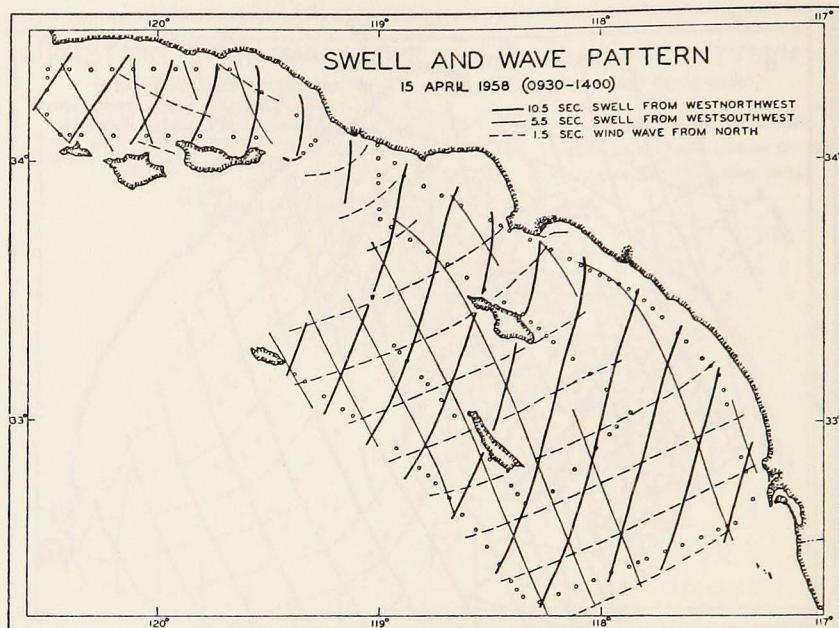


Figure 3. Survey of 15 April 1958. Flown aboard P5M at 2000 feet.

SIGNIFICANCE

Knowledge of the pattern of wave trains off southern California has several practical applications. Waves off Point Conception at the northwestern limit of the surveys are notoriously high compared with their progressively lower height farther southeast. This is not merely the result of the known diminution of wind velocity southeastward, because at least the 10-second swell is too long to have a local origin. Instead, the southeastward decrease in swell height must be due partly to protection offered by the islands which reflect much of the wave energy. The changing relationship of the various wave trains in the region must also produce changes in the character of wave recordings made at various places along the coast and for different times at the same site.

Ditching tests for airplanes at sea have shown that the best landing direction is parallel to the wave crests and troughs (Anonymous, 1953). As a result, a 30° or 210° true course is generally considered best for ditching in this region, because it is parallel to the

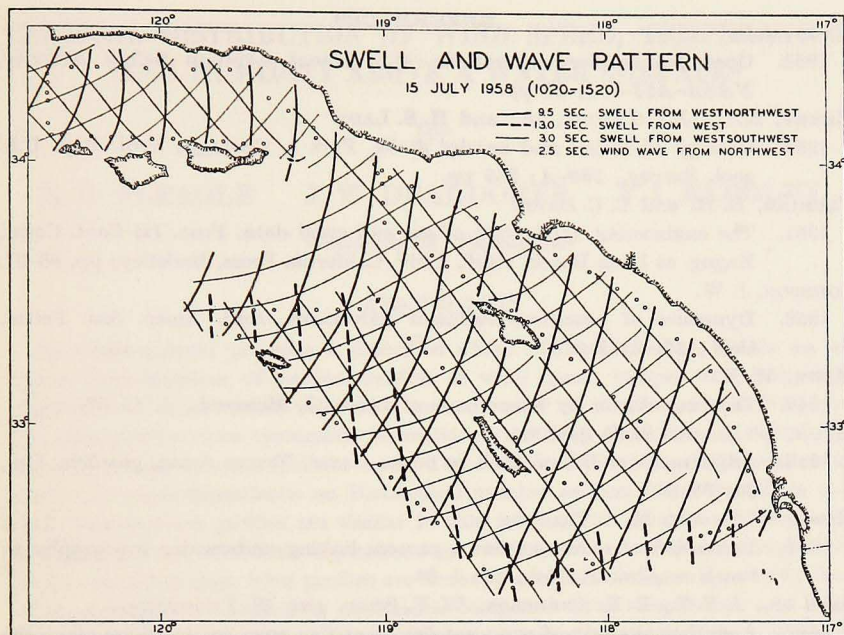


Figure 4. Survey of 15 July 1958. Flown aboard P5M at 400 feet because of low ceiling.

large main swell. However, a secondary swell from the west or southwest forms a crossing pattern that might damage an airplane landing along the main swell. If time permitted, an easier landing might be made on the lee side of the large islands that prevent access of some secondary swells.

The main swell from the westnorthwest is the one that contains the most energy. As it drives along the coast it is refracted so that it approaches nearly directly shoreward. Since at least a small angle remains, the wave, after breaking, drives ashore in such a direction as to carry some sand southeastward. The general southeastward movement of beach sand, locally contrary to the direction of offshore currents, is attested by the accumulation of as much as 280,000 yd³/year behind breakwaters and against groins of sandy beaches (Johnson, 1956). During times when storm waves approach from the south or when the long swell comes from the southern hemisphere, the drift may be reversed locally (Shepard, 1950), but the prevalence of the main swell requires a net southeastward movement of sand along the mainland shore.

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